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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1526

Part of Journal of Research of the National Bureau of Standards, Volume 30, March 1943

OCCURRENCE OF SUCROSE AND INULIN-HYDROLYZING ENZYMES IN COMMERCIAL ENZYME PREPARATIONS

By William Ward Pigman

ABSTRACT

The relative enzyme content of enzyme preparations which hydrolyze sucrose and inulin was determined for 14 enzyme preparations representing the principal commercial types available. Those of fungal origin seem invariably to contain invertases in about 0.5 to 1.0 percent of the quantities in commercial purified yeast invertase preparations. Enzyme preparations from plant sources (wheat, almond, and malt), from animal tissues (pancreases), and from *Bacillus mesentericus* had negligible contents of invertase. Enzyme preparations from *Aspergillus niger* and yeast exhibited considerable ability to hydrolyze inulin, those from *Aspergillus oryzae* and *A. flavus* exhibited some slight activity, and preparations from other sources were essentially inactive. For several representative enzyme preparations, the rate of hydrolysis of inulin and sucrose was studied and found to approximate a first-order reaction. The activity of the inulase in several *A. niger* enzyme preparations was found to be greatest in the range pH 3 to 4. Invertase preparations from *A. niger* were most active at pH 3 to 4 and those from *A. oryzae* at pH 5.0 to 5.5.

The results are considered from the viewpoint of the Weidenhagen theory, and it is shown that the original theory is incompatible with the present results in that either the invertases and inulases are different enzymes or they represent a class of enzymes (fructofuranosidases) in which the individual members vary according to the source. Thus the ratio of invertase to inulase activity varies from about 5 for the *A. niger* preparations to more than 4,000 for the yeast preparation. Following the suggestion of Helferich, the term "emulsin" is used as a synonym for a crude mixture of enzymes.

It is shown that the *A. niger* emulsins hydrolyze juices from the jerusalem artichoke, which contain levulose polysaccharides. This reaction may be useful for the commercial production of levulose from this source, as enzymic hydrolysis has certain advantages that may offset the high cost of the enzyme preparation.

Consideration is given to the different methods available for expressing enzyme activity. It is shown, for the enzymes reported in the present paper, that the pseudo first-order reaction constant is proportional to the enzyme concentration over a fairly wide range, and that this constant may be utilized for the expression of the enzyme content of various emulsins. Since the substrate concentration must be specified, it is suggested that the concentrations proposed by Weidenhagen be generally accepted, and that his standard conditions of temperature, etc., also be adopted.

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I. INTRODUCTION

For more than a century it has been known that many materials of biological origin contain catalysts for hydrolytic and oxidative reactions. These biological catalysts, or enzymes, should be of considerable commercial interest because of the mild conditions of temperature, pressure, and acidity under which many of them have their optimal activity. They have found limited application in industrial practice,[1] but their widespread use has been retarded by the lack of knowledge of the many problems involved. Some of the more important problems that have not received systematic study are the distribution of enzymes in natural products, sources of high activity, and the identity or nonidentity of enzymes from different sources which catalyze the same reactions. The present investigation attempts to provide this information for two enzymes, invertase and inulase.

Convenient and important sources of enzymes are the enzyme preparations manufactured for industrial and scientific purposes. These "emulsins"[2] are mixtures of enzymes of various types and are obtained from plant seeds, animal organs, and microorganisms. Some of the well-known products of these types are Malt diastase, Pancreatin, Takadiastase, yeast invertase. Pectinol, Polidase, and Mylase. These and other semicommercial and experimental preparations were studied in the present investigation for their invertase and inulase content.

The use of these enzyme preparations for the present work involved a number of uncertainties, arising particularly from the lack of information of their origin and manufacture, and the results obtained can be considered only as representative of the types of preparations available. The active content of enzyme preparations may be expected to vary from time to time for the same product unless the activity has been standardized by the manufacturer. Where the development of a particular use makes it desirable, it is probable in many instances that the activity may be increased as much as 10 to 100 times by controlling conditions and choosing active strains of microorganisms. It is believed that these difficulties are balanced by the ready availability of the products. Also, in most cases, the main variable is the particular strain of microorganism employed, which frequently is difficult for other investigators to obtain. The

[1] R. A. Gale, Wallerstein Lab. Comm. **4**, 112 (1941); L. Wallerstein, Ind. Eng. Chem. **31**, 1218 (1939).

[2] Helferich has been using the term "emulsin" to mean a mixture of glycosidic hydrolyzing enzymes obtained by the partial purification of plant extracts. Coffee emulsin is a mixture of enzymes obtained from the coffee bean, and yeast emulsin is synonymous with crude-yeast invertase. See B. Helferich and F. Vorsatz, Z. physiol. Chem. **237**, 254 (1935). To some writers the term "emulsin" has meant almond emulsin or even the β-glucosidase therein, but Helferich's usage would seem to be preferable. In the present paper, however, the term "emulsin" is broadened further to include all mixtures of enzymes and is synonymous with "crude or partially purified mixtures of enzymes." It might be noted that a dictionary definition of "emulsin" is "an enzyme preparation obtained from certain fungi and several of the higher plants, notably almonds, and prepared as a white amorphous mass." See Webster's New International Dictionary, second edition (G. and C. Merriam Co., Springfield, Mass., 1939).

information available about the various enzyme preparations is given in section VII, p. 171.

The inulase content was investigated because of the interest of the National Bureau of Standards in the production of levulose from polysaccharides of the inulin type contained in Jerusalem artichoke and dahlia tubers and a number of other plants.[3]

The invertase content was studied to determine the possibility of a correlation with the inulase activity as demanded by the original Weidenhagen theory.

One of the outstanding characteristics of enzymes is the specific nature of their catalytic actions. Very slight changes in the substrate molecule often suppress the catalytic action considerably or even completely. This property is of considerable interest for the analysis of plant materials, which are often complex mixtures. The well-known method for the determination of raffinose in the presence of sucrose [4] depends on the selective actions of α-galactosidase and invertase. Other methods utilizing the procedure of Bourquelot [5] should be feasible for determining the composition of mixtures such as those containing starch, hemicelluloses, etc. However, as a preliminary requisite for analyses of this type, the occurrence of the necessary enzymes must be established, and a knowledge of the other enzymes in the same emulsins must be obtained. The present investigation is a start in this direction, and provides data for developing selective methods for the analysis of mixtures of inulin and sucrose and possibly of other polysaccharides.

II. EXPRESSION OF ENZYME ACTIVITY

1. STANDARD CONDITIONS

Since many methods have been suggested for the determination of enzyme activity, particularly invertase activity,[6] the choice of any one method is arbitrary. One of the greatest sources of difficulty in the comparison of different methods is that different conditions of substrate concentration, temperature, pH, etc. are specified by the various investigators. Weidenhagen has specified [7] a set of standard conditions ("Normalbedingungen"), which, because of their widespread applicability, it seems desirable to adopt until more favorable conditions have been found. The exact conditions are given in the following quotation, which is cited here in the original language to avoid any possibility of mistranslation.

"Man löst 2.500 g Maltose oder die äquivalente Menge eines anderen Substrates bei optimalem pH und 30° C unter Zusatz des entsprechenden Enzyms in 50 cm^3 Gesamtvolumen und ermittelt in zu bestimmten Zeiten genommenen Proben den Grad der Hydrolyse."

The standard substrates to be used for several important enzymes are given as maltose (α-glucosidase), salicin (β-glucosidase), melibiose (α-galactosidase), lactose (β-galactosidase), and sucrose (invertase),

[3] R. F. Jackson, C. G. Silsbee, and M. J. Proffitt, BS Sci. Pap. **20**, 587 (1926) S519; Facts about Sugar **21**, 32[6] (1926); F. J. Bates, Sugar **28**, 167 (1926); NBS Letter Circular LC 500 (1937); M. J. Proffitt, J. A. Bogan, and R. F. Jackson, J. Research NBS **19**, 263 (1937) RP1025; R. F. Jackson and J. A. Mathews, J. Research NBS **15**, 341 (1935) RP832.

[4] C. S. Hudson and T. S. Harding, J. Am. Chem. Soc. **37**, 2193 (1915); H. S. Paine and R. T. Balch, J. Ind. Eng. Chem. **17**, 240 (1925), J. Am. Chem. Soc. **49**, 1019 (1927).

[5] See review by Béguin, Pharm. Acta Helv. **1**, 65, 90 (1926).

[6] See review by C. A. Browne and F. W. Zerban, Sugar Analysis, p. 434 (John Wiley & Sons, Inc., New York, N. Y., 1941).

[7] Nord-Weidenhagen, Handbuch der Enzymologie, p. 538 (Akademische Verlagsgesellschaft, Leipzig, 1940).

all as indicated above to be at a concentration of 0.1388 *M* in the reaction mixture, at the optimal pH and at a temperature of 30° C. For inulin, the suggested concentration is 1.125 g of anhydrous inulin in 50 ml of solution. The standard concentration applies only to substances of known structure and molecular weight, and for inulin and other polysaccharides, arbitrary concentrations must be employed.

In addition to the conditions specified by Weidenhagen, several other variables need to be controlled. It is well known that both the nature of the buffer and its concentration affect the rate of enzyme reactions.[8] Acetate and phosphate buffers have been used more extensively for this purpose, and it is now suggested that the solution in which the hydrolysis takes place be 0.160 *M* in acetate buffer or 0.04 *M* in phosphate buffer. These concentrations are easily obtained by diluting four volumes of Walpole 0.2 *M* acetate buffers with one volume of water (or enzyme solution) or by diluting the Clark and Lubs phosphate buffers (0.05 *M*) in the same proportion. It is also suggested that, when possible, sugar determinations by chemical methods be employed to follow the reactions rather than polariscopic methods, since, under the standard conditions, the rotational changes are rather small for the disaccharides.

In his extensive study of the effects of the structures of glycosides on the rate of enzymic hydrolysis, Helferich has adopted a substrate concentration of 0.052 *M*, but the other conditions are the same as those used by Weidenhagen. In specificity studies, and in those instances where the rarity of the substrates or other factors make it desirable to use lower concentrations of substrates than 0.1388 *M*, it is suggested that 0.052 *M* be adopted. However, when the enzymic activities are being measured, the more concentrated solutions should be used.

2. METHODS FOR EXPRESSING ACTIVITY

For the expression of enzyme activity, the situation is confused. Most methods depend on the assumption that the hydrolysis of the substrate (e. g., of sucrose by invertase) follows the first-order equation, but since the reaction constant calculated in this manner is affected greatly by the initial concentration of the substrate, the substrate concentration must be fixed arbitrarily. The assumption that a monomolecular "k" may be calculated is disputed by some investigators,[9] but since no satisfactory method for *general* use has been developed without this assumption, no alternative remains at present.[10]

As shown in table 1, the hydrolysis of inulin and sucrose by fungal enzymes appears to follow the first-order equation within a deviation of ±10 percent from the average. Most earlier measurements seem to fall within this range, and it is the opinion of the writer that additional careful investigation is necessary before this point can be considered as settled. It seems possible that by choice of a suitable

[8] W. A. Wisansky, J. Am. Chem. Soc. **61**, 3330 (1939); S. Veibel and H. Lillelund, Enzymologia **9**, 161 (1940).

[9] W. R. Johnston, S. Redfern, and G. E. Miller, Ind. Eng. Chem., Anal. Ed. **7**, 82 (1935).

[10] Several excellent discussions of enzyme kinetics in relation to methods for the measurement of the activity of enzymes are given by O. Bodansky, J. Biol. Chem. **120**, 555 (1937), and by D. D. Van Slyke, Advances in Enzymology, p. 33 (Interscience Publishers, New York, N. Y., 1942). An alternative method of expressing activity might be developed by choosing substrate concentrations high enough that the hydrolysis would be of zero order, i. e., the velocity of hydrolysis would be independent of the substrate concentration for a considerable part of the reaction. The low solubility of some of the sugars and derivatives would limit the general application of this method, and in any case the Weidenhagen substrate concentrations are too dilute for the method to be applied.

substrate concentration, conditions may be found for many enzymes so that the reaction may be expressed by the first-order equation, although it should be noted that the reaction is not of the first order, since it is not independent of the substrate concentration.

For the present investigation, the assumption is made that for a fixed initial substrate concentration, the hydrolytic reaction follows the first-order equation (really the "die away" equation, see footnote 10), and the reaction constant may be used as a measure of the activity. Since measurements at the beginning of the reaction are probably less accurate than those at later times, and to minimize the inhibiting effects of products of the hydrolysis, the activity measure-

TABLE 1.—*Kinetics of hydrolysis of inulin and sucrose by fungal enzymes*

Time	Hydrolysis	$k \times 10^4$	Time	Hydrolysis	$k \times 10^4$
		INULIN			
T=30.0° or 50.0° C; pH=4.1; acetate-ion concentration=0.2 M; 1.013 g of anhydrous inulin in 50 ml of reaction mixture					
A. oryzae emulsin No. 1 (T=30.0° C; g=0.251 g)			*A. niger* emulsin No. 1 (T=30.0° C; g=0.218 g)		
Min.	*Percent*		*Min.*	*Percent*	
134	10.4	[a] (3.6)	100	24.0	11.9
210	17.1	[a] (3.9)	160	37.3	12.7
310	25.6	4.1	240	51.6	13.1
500	37.6	4.1	310	61.3	13.3
618	46.6	4.4	390	70.7	13.7
776	55.2	4.5	600	84.9	[a] (13.7)
1,440	78.9	4.7	1,455	98.2	
3 days	99.2				
Avg		4.4	Avg		12.9
A. oryzae emulsin No. 1 (T=50.0° C; g=0.251 g)			*A. niger* emulsin No. 2 (T=30.0° C; g=0.256 g)		
40	7.8	[a] (8.8)	100	5.3	
70	14.4	[a] (9.6)	240	13.8	[a] (2.7)
130	26.3	10.2	380	21.8	2.8
200	38.9	10.7	605	32.0	2.8
290	53.0	11.3	1,440	64.4	3.1
365	61.1	11.2	1,820	72.9	3.1
			4 days	96.4	
Avg		10.8	Avg		3.0
		SUCROSE			
Sucrose concentration: 2.375 g in 50 ml of reaction mixture; pH=4.5 (acetate-ion concentration=0.16 M)					
A. niger emulsin No. 1 (T=30.0° C; g=0.0438 g)					
30	8.6	[a] (13.0)			
70.4	19.2	[a] (13.2)			
130	32.7	13.2			
190	43.7	13.1			
250	53.6	13.3			
320.5	63.3	13.6			
398	70.8	13.4			
26 hr	100.6				
Avg		13.3			

[a] The values in parentheses were not considered in obtaining the average values.

ments were carried out in the interval 30- to 50-percent hydrolysis in most instances. By limiting this interval still more, it should be possible to minimize the effects of deviations from the first-order equation but at the expense of increasing the difficulties of analysis.

Another assumption generally made is, that the reaction constant is proportional to the amount of enzyme present, that is, k/(enzyme quantity) remains constant. This seems to be at least approximately true in most instances. In table 2, it is shown that for the hydrolysis of inulin by *A. niger* emulsin the quotient k/g (where g is grams of enzyme in 50 ml of reaction mixture) exhibits an insignificant variation of about 10 percent when the enzyme quantity (g) is varied twentyfold. A fiftyfold change in invertase concentration produces practically no change in the k/g ratio for sucrose hydrolysis by *A. niger* emulsin No. 1, although an appreciable effect is observed for a hundredfold change of enzyme concentration.

TABLE 2.—*Influence of enzyme concentration, enzyme stability, and effect of filtration of inulase and invertase of A. niger emulsin No. 1*

Time	Hydrolysis	$k \times 10^4$	g	$(k/g) \times 10^4$	Remarks
			INULASE		
			T=30.0° C; pH=4.0; inulin concentration 1.013 g in 50 ml of reaction mixture		
			Influence of Enzyme Concentration		
min	*Percent*				
80	41.1	28.7	0.542	53	Solution 0.2 M in acetate ion.
90	41.2	25.6	.464	55	
450	39.2	4.80	.093	52	
1,570	37.2	1.29	.0271	48	
			Stability [1] and Influence of Filtration [2]		
120	55.7	29.5	0.438	67	Filtered enzyme solution used.
120.3	54.0	28.0	.438	64	Unfiltered enzyme solution used.
121.3	59.7	32.5	.438	74	Filtered enzyme solution used after 7 days at 30° C.
121	57.7	30.9	.438	71	Unfiltered enzyme solution used after 7 days at 30° C.
					Acetate concentration in all the experiments was 0.16 M.
			INVERTASE		
			T=30.0° C; pH=4.5 (solution 0.16 M in acetate ion)		
			Influence of Enzyme Concentration		
19	43.6	131	0.438	300	Sucrose concentration was 2.375 g in 50 ml.
190	43.7	13.1	.0438	300	
965	44.6	2.66	.00876	300	
1,790	36.2	1.09	.00438	250	
			Stability [1] and Influence of Filtration [2]		
15.0	43.4	165	0.438	380	Filtered enzyme solution used.
15.0	41.2	154	.438	350	Unfiltered enzyme solution used.
15.0	45.5	176	.438	400	Filtered enzyme kept at 30° C for 7 days.
15.0	42.5	160	.438	370	Unfiltered enzyme kept at 30° C for 7 days.
					Sucrose concentration in all the experiments was 1.900 g in 50 ml.

[1] The filtered and unfiltered solutions of footnote 2 were kept at 30° C for 7 days and then analyzed.
[2] The enzyme preparation was made up to volume with water, and a portion was filtered before analysis.

The results given in table 2 indicate that there is a slight increase (evaporation?) rather than a loss of activity as a result of keeping aqueous solutions of the *A. niger* emulsin for 7 days at 30°C when covered with a layer of toluene. It is possible that the buffered solutions (pH 4.0 to 4.5) used for the measurement of the effect of enzyme concentration may have produced some inactivation and that this may explain the decrease in the k/g ratio observed for the longer time intervals in these experiments. It is also shown in the table that the insoluble material has no significant effect on the reaction.

In the present paper the measurement of the activity of the enzymes studied depends on the applicability of the first-order equation and on the constancy of the k/g ratio. For the actual expression of activity, a quantity called the enzyme value (EV) is used and is defined as $EV=k/(g\times\log 2)$, where k, the reaction constant under the Weidenhagen conditions of temperature and substrate concentration, is calculated by the first-order equation $k=(1/t)\log(100/100-X)$, t is the time in minutes corresponding to X-percent hydrolysis, and g is the weight of enzyme in 50 ml of reaction mixture. The enzyme value is then the reciprocal of the time for 50-percent hydrolysis of the substrate for an emulsin concentration of 1 gram in 50 ml of solution. For calculating k, Briggsian logarithms are used, but any base may be used for the enzyme value as long as k and log 2 are expressed similarly.

If the unit of enzyme quantity is taken as the amount of pure enzyme in 50 ml of reaction mixture, which, under the standard conditions of Weidenhagen, produces a reaction constant, $k=\log 2$, then the enzyme value is equal to the number of enzyme units per gram of crude preparation. These arbitrary units are referred to hereafter as Weidenhagen units. Pringsheim and Ohlmeyer[11], define the Pringsheim inulase unit as the amount of enzyme which produces 30-percent hydrolysis of 150 mg of inulin in 1-percent solution in 3 hours at 37° C. A comparison of this unit with the Weidenhagen unit, as previously defined, was made. The results in table 3 show that the enzyme preparation, which has an inulase value of 0.0174 (0.0174 units per gram), contains 35 Pringsheim units per gram. The Weidenhagen unit is then about 2,000 times larger than the Pringsheim unit. The table also shows that the inulin concentration used in the present investigation gives the same results, within the experimental error, as that used by Weidenhagen. However, in future work, it is intended to return to the Weidenhagen concentration.

TABLE 3.—*Comparison of inulase units*

[Enzyme concentration=0.218 g of *A. niger* emulsin No. 1 in 50 ml of reaction mixture]

Inulin concentration	Temperature	Time	Hydrolysis	$k\times 10^4$	EV	Pringsheim units per gram	Remarks
	°C	Min.	Percent				
1.125	30.0	248	47.9	11.4	0.0174	----------	Weidenhagen conditions.
1.013	30.0	248	49.2	11.9	.0181	----------	Conditions in this paper.
0.500	37.0	162	52.3	19.8	--------	[a] 35	Pringsheim conditions.

[a] One Pringsheim unit corresponds to $k=0.00086$. Since 0.150g of inulin corresponds to 15 ml of 1-percent solution, the enzyme unit is based on this volume and $g=0.218\times 0.3$. The number of Pringsheim units is given by

$$\frac{0.00198}{0.00086\times 0.218\times 0.3}=35.2.$$

[11] H. Pringsheim and P. Ohlmeyer, Ber. deut. Chem. Ges. **65**, 1242 (1932).

Many different measures of enzyme activity have been employed for the carbohydrases. Although most methods depend on the constancy of the k/g ratio, the experimental conditions of substrate concentration, temperature, etc., are so different that it is difficult to compare the reported activities. In an effort to clarify somewhat a very confusing situation, table 4 has been prepared to illustrate the differences between some of the more important methods.

TABLE 4.—*Methods for the expression of glycosidase activity*

Name	Formula for expressing activity[a]	Substrate concentration	Temperature of measurement	Volume used to express emulsin concentration	References[b]
		Moles/liter	°*C*	*ml*	
Enzymwert, or enzyme value	$EV=\frac{k}{g\times\log 2}$	0.1388	30	50	1
Wertigkeit, or enzyme efficiency.	$W=EE=\frac{k}{g\times\log 2}$	.0520	30	50	2
Xf	$Xf=\frac{k(S)}{g}$				3
Salicin spaltungsfähigkeit	$Sal.\ f=\frac{k}{g}$	.070	30	50	4
		.139	30	50	5
k value	$k\ \text{value}=\frac{100\,k}{g_1}$	.00730	20	100	6
Time value (Zeitwert)	$t_0=\frac{0.6154\times g_2}{k}$	.467	15.5	500	7,8
Saccharase-Wert	$SW=\frac{1}{t_0}=\frac{k}{0.6154\times g_2}$	.467	15.5	500	8,7

[a] Explanation of symbols:
k=monomolecular reaction constant (Briggsian logarithms).
g, g_1, and g_2=grams of emulsin in indicated volume.
(S)=initial substrate concentration.

[b] REFERENCES

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8. R. Willstätter and R. Kuhn, Ber. deut. Chem. Ges. **56**, 569 (1923).

III. INVERTASE CONTENT OF ENZYME PREPARATIONS

Table 5 summarizes the results obtained for the invertase activity of 14 enzyme preparations. The seven emulsins of fungal origin exhibit considerable ability to hydrolyze sucrose, but the most active of these has only about 1 percent of the activity of a commercial yeast invertase (yeast emulsin No. 1). It is interesting to note that the total variation in invertase activity of the fungal preparations is only some sevenfold, and since the least active of these contained a diluent, the variation is still less.

The one bacterial emulsin investigated showed a negligible invertase content, and the pancreatic extracts are similar in this respect. The wheat, malt, and almond emulsins exhibited a very slight invertase activity.

TABLE 5.—*Invertase content (EV) of enzyme preparations*

[Sucrose concentration=2.375 g in 50 ml of reaction mixture; T=30° C.]

Enzyme preparation	pH=4.5 (approx); acetate-ion concentration=0.2 M				pH=6.7 (approx); phosphate concentration=0.05 M			
	Time	Hydrolysis	g	$EV\times10^4$	Time	Hydrolysis	g	$EV\times10^4$
	min	*Percent*			*min*	*Percent*		
A. oryzae emulsin No. 1	110	55.0	[a]0.251	420	224	49.4	[a]0.501	88
A. oryzae emulsin No. 2	73	29.6	.563	120	97	35.8	.563	120
A. oryzae emulsin No. 2 (purified)	50	32.6	.563	200	80	36.8	.563	150
A. oryzae emulsin No. 3	45.6	43.7	.563	320	79	42.5	.563	180
A. niger emulsin No. 1	46	48.4	[a].218	950	268	37.4	[a].218	120
A. niger emulsin No. 2	121	41.2	[a].256	250	231	41.1	[a].511	65
B. mesentericus emulsin No. 1	1,500	(.3)	.563	(.05)	1,440	(.3)	.563	(.05)
Wheat emulsin No. 1	1,380	.6	.563	.11	1,440	(.3)	.563	(.05)
Malt emulsin No. 1	1,440	9.1	.563	1.7	1,440	1.7	.563	.3
Almond emulsin No. 1	1,440	7.5	[a].400	2.0	1,440	6.4	[a].400	1.7
Pancreatic emulsin No. 1	1,440	(.3)	.563	(.05)	1,440	(.3)	.563	(.05)
Pancreatic emulsin No. 2	1,440	(.3)	.563	(.05)	1,485	4.0	.563	0.7
Yeast emulsin No. 1	30	36.8	.00257	86,000	70	47.7	.00257	52,000
Aspergillus emulsin No. 1	30	37.1	.563	400	62	45.5	.563	250
Yeast emulsin (Weidenhagen)	8	30.1	.020	32,000				

[a]Based on soluble material of emulsin.

With one exception (No. 1), the *Aspergillus oryzae* emulsins exhibit less variation in activity between the two hydrogen-ion concentrations at which the measurements were carried out than do the *Apergillus niger* emulsins. As demonstrated in table 6, this is to be ascribed to the difference in the optimal pH for the two classes of fungi. The pH optimum for the *A. niger* invertase seems to lie in the pH interval 3 to 4, and that for the *A. oryzae* invertase near pH 5.0. This property of the *A. niger* invertase may be of particular importance when it is desired to carry out the inversion of sucrose at acidities greater than that optimal for yeast invertase. The *A. oryzae* emulsin No. 1 behaves more like the *A. niger* emulsins, but whether this may be due to an incorrect classification cannot be stated at present. The *Aspergillus* emulsin No. 1 seems to be similar in properties to the *A. oryzae* emulsins.

TABLE 6.—*Effect of* pH *on activity of invertases*

[Sucrose concentration=2.376 g in 50 ml of reaction mixture; acetate-ion concentration=0.16 M; T=30.0° C.]

A. niger emulsin No. 1 g=0.0438 g in 50 ml				*A. oryzae* No. 2 (purified) g=0.282 g in 50 ml			
pH	Time	Hydrolysis	$(k/g)\times10^4$	pH	Time	Hydrolysis	$(k/g)\times10^4$
	min	*Percent*			*min*	*Percent*	
3.0	157.5	47.4	400	4.0	80	26.3	59
4.0	170	48.6	390	4.5	80	28.6	65
4.45	195	50.1	350	5.0	80	30.0	69
5.0	180.5	38.5	270	5.5	80	29.8	68

The hydrolysis of sucrose by *A. oryzae* emulsin (Takadiastase) was studied by Weidenhagen,[12] and the results are in agreement with those of the present investigation in indicating that the optimal pH is around 5.0.

[12] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. 78, 125 (1928).

The kinetics of the hydrolysis of sucrose by the invertase in commercial Takadiastase have been investigated.[13] It was claimed that the reaction proceeds more slowly than demanded by the first-order equation (decreasing reaction constants), and that the hydrolysis of sucrose by yeast invertase proceeds more rapidly than required by the first-order equation (increasing reaction constants). It is shown in table 1 that the hydrolysis by the *A. niger* emulsin follows the first-order equation fairly closely. As previously mentioned, however, the writer believes that this problem requires additional investigation before the kinetics can be known with certainty.

IV. INULASE CONTENT OF ENZYME PREPARATIONS

It has been known from earlier work that emulsins from *A. niger* have considerable ability to hydrolyze inulin to levulose.[14] Commercial yeast emulsin (invertase) also is known to catalyze the hydrolysis of inulin, [15] and numerous references of a qualitative nature are to be found on the occurrence of inulases in various fungi.[16]

The results of the present investigation are in agreement with this previous work, as table 7 demonstrates. The *A. niger* emulsins and the *A. oryzae* emulsin No. 1 have considerable inulase activity, and the other *Aspergillus* emulsins have a slight but definite activity. As was pointed out for the invertase activity, the *A. oryzae* emulsin No. 1 resembles those for the *A. niger* preparations rather than the other *A. oryzae* preparations. The plant, bacterial, and pancreatic emulsins exhibit no appreciable inulase activity.

TABLE 7.—*Inulase content of enzyme preparations*

[Inulin concentration=1.013 g, of anhydrous inulin in 50 ml of reaction mixture; T=30.0° C.]

Enzyme preparation	pH=4.5 (approx) (acetate buffer)				pH=6.5 (approx) (phosphate buffer)				Ratio [c]: Invertase value / Inulase value
	Time	Hydrolysis	g	[d] $EV \times 10^6$	Time	Hydrolysis	g	[d] $EV \times 10^6$	
	Min	*Percent*			*Min*	*Percent*			
A. oryzae emulsin No. 1	1,440	[a] 78.9	[b] 0.251	[a] 5800	1,440	30.7	[b] 0.501	740	7.2
A. oryzae emulsin No. 2	1,440	2.7	1.13	24	1,440	1.5	1.13	13	500
A. oryzae emulsin No. 2 (purified)	1,440	2.7	1.13	24	1,440	(0.7)	1.13	(6)	830
A. oryzae emulin No. 3	1,440	15.1	1.13	150	1,440	8.6	1.13	80	210
A. niger emulsin No. 1	600	[a] 84.9	[b] 0.218	[a] 19,700	1,440	67.6	[b] 0.437	2,600	4.8
A. niger emulsin No. 2	1,440	[a] 64.4	[b] .256	[a] 3,900	1,440	27.2	[b] .511	620	6.4
Aspergillus emulsin No. 1	1,500	3.5	.563	61	1,440	5.8	.563	110	660
Yeast emulsin No. 1	1,465	40.8	.257	2,000	1,440	12.9	.257	540	4,300
B. mesentericus emulsin No. 1	1,440	(0.7)	1.13	(6)	1,440	(0.7)	1.13	(6)	.....
Wheat emulsin No. 1	1,440	(.7)	1.13	(6)	1,440	(.7)	1.13	(6)	.....
Malt emulsin No. 1	1,440	1.6	1.13	14	1,440	(.7)	1.13	(6)	.....
Almond emulsin No. 1	1,440	(.7)	0.803	(9)	1,440	(.7)	0.803	(9)	.....
Pancreatic emulsin No. 1	1,440	(.7)	.564	(13)	1,440	(.7)	1.13	(6)	.....
Pancreatic emulsin No. 2	1,440	(.3)	.563	(5)	1,440	(.3)	0.563	(5)	.....

[a] These values are from data in table 1 and are for pH=4.0. The enzyme value is the average value.
[b] Based on soluble material.
[c] Calculated from values in this table and table 5 for pH=4.5 or 4.0.
[d] Parenthesis indicate maximum values calculated on the basis of a maximum iodine consumption of 0.3 ml.

[13] R. Weidenhagen and B. Dey, Z. Ver. deut. Zucker-Ind. **78**, 242 (1928).
[14] H. Pringsheim, and W. G. Hensel, Ber. deut. Chem. Ges. **64**, 1431 (1931); H. Pringsheim and P. Ohlmeyer, Ber. deut. Chem. Ges. **65**, 1242 (1932).
[15] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. **82**, 316, 912 (1932).
[16] A. C. Thaysen and L. D. Galloway, Microbiology of Starch and Sugars, p. 36 (Oxford University Press, London, 1930).

In agreement with Weidenhagen's earlier results, a commercial yeast emulsin (yeast invertase preparation), has a considerable inulase content, which seems to be about one-seventh of that in the most active *A. niger* material. The enzyme value of the yeast emulsin used by Weidenhagen may be calculated from his data, since very similar conditions were used. Using an average "*k*" as 0.0019 (see p. 914 of reference in footnote 15), the inulase value is calculated as $63{,}000 \times 10^{-6}$ for a yeast emulsin which had received considerable purification (invertase value=β-h-Fructosidase-Wert=333, as compared to values of 3 to 9 for commercial yeast invertases).

The optimal pH for the inulase action of the *A. niger* emulsins and the *A. oryzae* emulsin No. 1 is less than pH 4 and probably is around pH3 (see table 8). The lowest pH values are for the enzymes in 0.2 *M* acetic acid solution. The measurements could not be carried into the more acid region without changing the nature of the buffer. It is of interest that the optimal pH is near the region of maximal stability of levulose, pH 3.3.[17]

TABLE 8.—*Effect of* pH *on activity of inulases*

[T=30.0° C]

A. oryzae emulsin No. 1. Inulin concentration=1.013 g in 50 ml of reaction mixture. Acetate-ion concentration=0.20 *M*. g=0.250 g of enzyme in 50 ml of reaction mixture.			*A. niger* emulsin No. 1. Inulin concentration=0.810 g in 50 ml of reaction mixture. Acetate-ion concentration=0.16 *M*. g=0.0871 g in 50 ml of reaction mixture.			*A. niger* emulsin No. 2. Inulin concentration=0.810 g in 50 ml of reaction mixture. Acetate-ion concentration=0.16 *M*. g=0.204 g in 50 ml of reaction mixture.		
pH	Hydrolysis after 24 hr	$k/g \times 10^4$	pH	Hydrolysis after 24 hr	$k/g \times 10^4$	pH	Hydrolysis after 24 hr	$k/g \times 10^4$
	Percent			*Percent*			*Percent*	
• 3.7	82.8	21	• 3.3	90.7	82	• 3.3	64.0	15
4.1	82.2	21	4.1	87.1	71	4.1	61.7	14
4.6	79.6	19	4.5	86.2	69	4.5	60.6	14
5.1	74.0	16	5.0	80.2	56	5.0	52.2	11

• The reaction mixture, made up, using 0.2 *M* acetic acid, had the indicated pH in the presence of the enzyme.

The rate of hydrolysis of inulin by three *Aspergillus* emulsins was studied, and the results are recorded in table 1. Within a deviation of less than 10 percent, the reaction appears to follow the first-order equation, particularly when degrees of hydrolysis less than 20 and more than 80 percent are eliminated.

A comparison of the inulase activity at 30.0° and 50.0° C, of the *A. oryzae* preparation (see table 1) shows that the reaction rate is accelerated about 2.5 times when the temperature is changed from 30.0° to 50.0° C. This corresponds to an activation energy of 8,900 cal.

V. ACTION OF INULASE ON EXTRACTS FROM JERUSALEM ARTICHOKES

Inulin and similar polysaccharides occurring in the tuber of the jerusalem artichoke (*Helianthus tuberosus*) and in the dahlia, chicory, burdock, goldenrod, and dandelion plants have shown considerable promise for the production of crystalline levulose [18] and for the produc-

[17] J. A. Mathews and R. F. Jackson, BS J. Research **11**. 619 (1933) RP611.

[18] R. F. Jackson, C. G. Silsbee, and M. J. Proffitt, BS Sci. Pap. **20**, 587 (1926) S519; F. J. Bates, Sugar **28**, 167 (1926); NBS Letter Circular LC500 (1937).

tion of fermentable and/or edible levulose sirups.[19] Most of the methods used depend on acid hydrolysis, although, as shown by the investigations of Jackson, McDonald, and Goergen,[20] purified inulin gives a mixture of sugars consisting of about 92 percent of fructose, 5 percent of nonreducing difructose anhydrides, and 3 percent of *D*-glucose. This loss of levulose, due to the formation of the difructose anhydrides and possibly of glucose, is disadvantageous not only in the direct loss sustained but also in lowering the purity.[21] Weidenhagen has reported that inulin is quantitatively hydrolyzed by yeast emulsin (yeast invertase preparations) to reducing sugars.[22] In the present investigation, hydrolyses of from 98.8 to 100.0 percent were observed. Within the experimental error, the hydrolysis seems to be complete.[23]

The results outlined for the pure inulin made it desirable to carry out the same experiments with juices from the jerusalem artichoke. These were prepared by pressing the artichokes in a hydraulic press, soaking the residue in hot water, and repressing. The juice, which contained 10.8 percent of dry substance (by refractometer), had a pH of 6.2 and a density of 1.039 at 20° C. After hydrolysis with 0.33 *M* hydrochloric acid for 60 minutes at 80° C, the juice contained 0.0944 g of reducing sugar per milliliter (calculated as levulose in undiluted, hydrolyzed juice). For the enzyme hydrolysis, 20 ml of juice was acidified to pH 4.2 with hydrochloric acid, 0.400 g of *A. oryzae* emulsin No. 1 added, and the solution diluted to 25 ml. After 72.5 hours at 30° C, the solution had 0.0983 g per milliliter of reducing sugar, and after 91 hours, 0.0975 g (calculated as levulose per milliliter of undiluted juice). These results indicate that the hydrolysis is practically quantitative, since for inulin itself, the enzymic hyrdolysis gives about 5 percent more reducing sugar than the acid hydrolysis. Although only of a preliminary nature, these experiments would seem promising for application to the large-scale hydrolysis of juices containing levulose polysaccharides. The commercial utilization would, however, depend on the cost of the enzyme preparation, although some allowance would have to be made for the higher yields of reducing sugar, the savings due to the smaller amounts of acids, lime, and heat required, and to the probable increase in ease of crystallization due to the milder conditions employed.

VI. COMPARISON OF INULASE AND INVERTASE ACTIVITY

Weidenhagen has presented a scheme for the classification of hydrolytic carbohydrases, which is of considerable value and has stimulated considerable research.[24] As originally stated, the system demanded that there be only one enzyme for each α- and one for each β-glycosidic type. One enzyme should hydrolyze all β-*D*-glucosides (β-glucosidase), one all α-*D*-glucosides (α-glucosidase), one all α-*D*-galactosides (α-galactosidase), etc. He considered the disaccharides as glycosides and that the same enzyme should hydrolyze related polysaccharides, disaccharides, and glycosides. The system required that β-glucosi-

[19] R. T. Wendland, E. Fulmer, and L. Underkofler, Ind. Eng. Chem. **33**, 1078 (1941); DT. Englis and H. A. Fiess, **34**, 864 (1942).
[20] E. J. McDonald and R. F. Jackson, J. Research NBS **24**, 181 (1940) RP1277.
[21] R. F. Jackson and J. A. Mathews, J. Research NBS **15**, 341 (1935) RP832.
[22] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. **82**, 316, 612 (1932).
[23] This agrees with the results found by M. Adams, N. K. Richtmyer, and C. S. Hudson, who have very kindly informed the writer of the unpublished results of their study of the action of purified yeast invertase on inulin.
[24] R. Weidenhagen, Ergebn. Enzymforsch. **1**, 168 (1932).

dase hydrolyze alkyl and aryl β-*D*-glucosides, cellobiose, and gentiobiose. Similarly, α-glucosidase should catalyze the hydrolysis of alkyl and aryl α-*D*-glucosides as well as maltose, and invertase (β-fructofuranosidase) should hydrolyze both sucrose and inulin.

In previous papers, evidence was given that the β-glucosidase and the β-galactosidase of almond emulsin probably hydrolyze the corresponding glycosides and disaccharides,[25] and the results obtained for the present series of preparations furnish additional information of interest in this connection.

A comparison of the invertase and inulase activities of the same enzyme preparations is made in the last column of table 7. In considering the comparison, it should be remembered that the conditions used for making the activity determinations are extremely arbitrary, and that for other conditions, the ratios are different. If the same part of the enzyme molecule is responsible for both the hydrolysis of inulin and sucrose, and if, as originally stated by Weidenhagen, there is only a single invertase, then the ratio of the invertase to inulase activity should be independent of the source of the material. The ratios in table 7, however, vary from about 5 for *A. niger* emulsins to more than 4,000 for yeast emulsin, and the other *Aspergillus* preparations fall between these extremes. According to unpublished work of M. Adams, N. K. Richtmyer, and C. S. Hudson, who have generously allowed their results to be quoted, highly purified baker's yeast invertase (enzyme value about 1,000) exhibits a ratio for these activities of 2,800 and a highly purified brewer's yeast preparation 28,300. The variation is then from about 5 to 28,000. These results agree with those previously obtained by other workers,[26] who have found that enzymes from different sources but hydrolyzing the same type of linkage have different specificities.

This evidence would seem to be ample proof that the unmodified Weidenhagen theory is untenable. The ascribing of these differences by Weidenhagen and Renner to variations in the "Träger" is not valid, as carbohydrates apparently do not dissociate[27] to yield coenzymes and carriers ("Träger"). Since the entire molecule must be termed the enzyme, appreciable changes in a part would produce a new molecule and, therefore, a new enzyme.

VII. EXPERIMENTAL PROCEDURE

1. ENZYME PREPARATIONS (EMULSINS)

Some of the emulsins studied in this investigation are principally commercial preparations developed specifically for enzymes not investigated in the present work, and others are purely experimental. Most of the information given was provided by the manufacturers, who also, in all instances, classified the microorganisms. Since the preparations are usually standardized for some particular enzyme activity other than that studied, it is quite probable that considerable variation may be expected for the emulsin prepared at different times. For all emulsins except those of pancreatic origin, the weights

[25] B. Helferich and W. W. Pigman, Ber. deut. chem. Ges. **72**, 212 (1939); W. W. Pigman, J. Research NBS **27**, 1 (1941) RP1398.

[26] H. Pringsheim, H. Borchardt, and F. Loew, Z. physiol. Chem. **202**, 23 (1931); B. Helferich and F. Vorsatz, Z. physiol. Chem. **237**, 254 (1935); K. Myrbäch and S. Myrbäch, Svensk Kem. Tid. **48**, 64 (1936); R. Weidenhagen and A. Renner, Z. Ver. deut. Zucker-Ind. **86**, 22 (1936).

[27] B. Helferich, R. Hiltmann, and W. Pigman, Z. physiol. Chem. **259**, 150 (1939).

(grams) in 50 ml of solution represent the soluble material of the preparation. For those containing appreciable quantities of insoluble material (*A. oryzae* No. 1, *A. niger* Nos. 1 and 2, almond emulsin No. 1), the soluble material was determined by filtering the aqueous enzyme solution and evaporating it to constant weight in a vacuum desiccator over calcium chloride. Except for emulsins which had been diluted with sugars, the reducing sugar equivalent (as glucose) varied from about 7 mg/g of emulsin to 70 mg/g. As a rule, the plant emulsins seem to have a higher reducing power than those from microorganisms or pancreases. In purchasing emulsins, it may be desirable to specify the diluent desired.

(a) EMULSINS FROM PLANT EXTRACTS

These are extracts of seeds, in some instances after a pretreatment, from which the enzymes have been precipitated. The malt emulsin is probably similar to the well-known commercial "Malt extract", for which the preparation is given in the U. S. Dispensatory.[28]

A review of the enzymes of barley has been made by Glick.[29]

Malt Emulsin No. 1.—(Malt diastase preparation, by courtesy of the Wallerstein Laboratories.) "The product was prepared from malt by extraction and salt precipitation. It was standardized to a Lintner value of 1,000, using sodium sulfate as a diluent. Contains a mixture of alpha and beta amylase and in addition small amounts of proteolytic enzymes." The material dissolves in water with only a slight residue.

Wheat Emulsin No. 1.—(Beta-Amylase, furnished by courtesy of the Wallerstein Laboratories.) "This is a preparation which was made from wheat by extraction and salt precipitation. It is substantially but not entirely free from alpha amylase. Lintner value 1,000, standardized to uniform Lintner strength, using sodium sulfate as diluent." A considerable quantity of insoluble material is present in the solid emulsin.

Almond Emulsin No. 1.—(Furnished by courtesy of B. F. Helferich, of the University of Leipzig.) This is the "Rohferment" of Helferich,[30] which is prepared from sweet almond kernels by zinc sulfate treatment and tannin precipitation. The composition of this material has been studied in recent years by Helferich and associates.[31] The solid emulsin contains about 71 percent of soluble material.

(b) EMULSINS FROM ANIMAL ORGANS

The present study includes only pancreatic preparations. These are probably similar in composition to the well-known "Pancreatin", for which the preparation is given in the U. S. Dispensatory.[32]

Pancreatic Emulsin No. 1.—(Degomma 160 A, furnished by the courtesy of the Röhm & Haas Co.) The manufacturer states: "Degomma 160 A is prepared from swine pancreas extract by selective precipitation. The Degomma 160 A has high amylase activity. It dissolves practically completely in water."

Pancreatic Emulsin No. 2.—(Pancreas Substance, obtained from Armour & Co.) The manufacturer states: "The material is manufactured from hog pancreas activated by the use of enterokinase from the hog duodenum. It is vacuum dried, defatted, and ground to a fine powder. The whole pancreatic gland is included in the product." A considerable quantity of undissolved material remains when the substance is shaken with water.

(c) EMULSINS FROM MICROORGANISMS

The general procedures followed in the preparation of enzyme mixtures from microorganisms are well known, but the details are

[28] 22d ed., p. 459 (J. B. Lippincott Co., Philadelphia, Pa. (1937)).
[29] D. Glick, Wallerstein Lab. Comm. 4, No. 11, 20 (1941).
[30] B. Helferich and S. Winkler, R. Gootz, O. Peters, and E. Günther, Z. physiol. Chem. 208, 91 (1932).
[31] B. Helferich, Ergebn. Enzymforsch. 7, 83 (1938).
[32] 22d ed., p. 808, J. B. Lippincott Co., Philadelphia, Pa. (1937).

usually trade secrets. The processes involved have been reviewed,[33] and the following may be considered a typical procedure.

Wheat bran to which nutrient substances have been added is sterilized by steam, and the moist material is placed in trays to a depth of about 1 inch. After inoculation with spores, the material is allowed to stand while the fungus grows. The temperature is controlled by passing air between the trays. When the optimal development has been attained, the mass is extracted with water and an extract containing 10 to 20 percent of solids if obtained. The enzymes and contaminating material are precipitated by the addition of alcohol or other material and dried in air.

For bacterial emulsins, the process is similar except that aerated solutions are frequently used and the enzymes are excreted directly into the nutrient medium, which, after separation of the bacteria, is treated similarly to the fungal extract to obtain the dry emulsin.

Aspergillus oryzae Emulsin No. 1.—(Maltase No. 16, furnished by courtesy of the Röhm & Haas Co.) This is a preparation developed for its α-glucosidase (maltase) activity and contains active amylases. It is produced from an active strain of *A. oryzae* and contains 89 percent of water-soluble material.

Aspergillus oryzae Emulsin No. 2.—(Fungal enzyme furnished by courtesy of the Wallerstein Laboratories.) "This is a highly active enzyme prepared from *Aspergillus oryzae* by extraction, purification, and salt precipitation. It has been standardized, using sodium sulfate as a diluent, to a Lintner value of 1,000 and ordinarily contains lactose as a carrier. It contains besides an amyolytic enzyme, considerable amounts of proteolytic enzymes, cytases, phosphatases, and maltase." The material is practically completely soluble in water.

Aspergillus oryzae Emulsin No. 2, purified.—(Mylase P for Thiamin determination, furnished by courtesy of the Wallerstein Laboratories.) "This represents a specially fractionated mixture from the same source as the above, and has been found to be rich in phosphatase, cytases, and hemicellulases, and contains some maltase." Since it is not known that this material represents solely the effects of purification of Emulsin No. 2, differences between the two emulsins cannot be considered as significant in this respect. The material is completely soluble in water.

Aspergillus oryzae Emulsin No. 3.—(Takadiastase purchased from the Takamine Laboratories.) This is crude undiluted takadiastase (970 percent) which, according to the literature, is prepared from *A. oryzae*. (I. Effront, Chem. et Ind. **43**, 3 (1904); J. Takamine, Ind. Eng. Chem. **6**, 824 (1914). The Takadiastase has been extensively studied by many workers.[34] The material dissolves with only a slight residue.

Aspergillus niger Emulsin No. 1.—(Cellulase No. 55, furnished by courtesy of the Röhm & Haas Co.) This preparation was developed for its cellulose hydrolyzing ability. The material contains 77 percent of water-soluble substance.

Aspergillus niger Emulsin No. 2.—(Enzyme 100 D purchased from the Röhm & Haas Co.) This is a commercial preparation from *A. niger*. Polygalacturonic acid is converted to galacturonic acid in high yield by the preparation.[35] Diatomaceous earth has been used as a diluent. The material contains 91 percent of water-soluble substance.

Aspergillus Emulsin No. 1.—(Polidase No. 566, furnished by courtesy of the Schwarz Laboratories.) The manufacturer reports the following enzymes to be present in considerable amounts: proteases, α-amylase, β-amylase, maltase, acid phosphatase, β-glucosidase, catalase, and nucleases. β-Galactosidase-(lactase), invertase, and lipase are reported in fair quantities; inulase, in small quantities; and urease, peroxidase, and carboxylase are absent. The emulsin dissolves in water to give a clear solution.

Bacillus mesentericus Emulsin No. 1.—(Special Rapidase, furnished by courtesy of the Wallerstein Laboratories.) "This represents an experimental preparation

[33] I. Effront, Chem. et Ind. **43**, 3 (1940); J. Takamine, Ind. Eng. Chem. **6**, 824 (1914); L. Wallerstein, Wallerstein Lab. Comm. No. 7, p. 5 (December (1939).

[34] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. **78**, 125, 243 (1928); K. Aizawa, Enzymologia **6**, 321 (1939); T. Harada, Ind. Eng. Chem. **23**, 1424 (1931), and many others.

[35] H. H. Mottern and H. L. Cole, J. Am. Chem. Soc. **61**, 2701 (1939); W. W. Pigman, J. Research NBS **25**, 301 (1940) RP1325.

of alpha-amylase (chiefly destrogenic) obtained from *B. mesentericus* by extraction and salt precipitation. The preparation is standardized to a definite starch liquefying power, a mixture of sodium chloride, sodium sulfate, and phosphates being used as diluent. The preparation contains appreciable amounts of bacterial proteolytic enzymes. Optimum pH range, 6.5 to 8.0; optimal temperature range, 65° to 70° C." It dissolves practically completely in water.

Yeast Emulsin No. 1.—(Invertase solution in 10-ml sealed glass vials.) Solid substance is 0.257 g in 10 ml of solution. For information on commercial invertase preparations, see review by L. Wallerstein.[36]

2. SUBSTRATES

Sucrose.—Standard Sample No. 17, Standard Sucrose, of the National Bureau of Standards was used. This material may be purchased from this Bureau.

Inulin.—A sample of once recrystallized inulin from dahlias was recrystallized twice from hot water (90° C) and dried in air. Moisture content as determined by drying to constant weight in high vacuum at 90° C was 7.7 percent. All weights recorded are calculated on an anhydrous basis. The optical rotation, on anhydrous basis, was $[\alpha]_D^{20} = -40.8$ (c, 1.2; water). In the preparation of inulin solutions, it was necessary to warm the solutions to 60° to 70° C to bring about dissolution and then to cool them to room temperature before making them to volume. Although supersaturated, the solution remains clear for several days.

3. BUFFER SOLUTIONS

Two types of buffer solutions were used. In the range pH 3 to 5.5, Walpole acetate buffers, made by mixing 0.2 *M* acetic acid and 0.2 *M* sodium acetate, were found satisfactory. For the measurements above pH 5.5, the Clark and Lubs phosphate buffers (0.05 *M*) were employed. The hydrogen-ion concentrations were measured with a glass electrode pH meter at 25° C. Since the enzyme preparations had considerable buffering action, the pH values recorded should be considered as only approximate. In all instances, buffer mixtures containing emulsin were measured and found to vary not more than 0.1 from that of the recorded value for the buffer alone. Two hydrogen-ion concentrations, pH=4.5 and 6.5, were chosen for the analyses of enzyme activity. Most enzymes are active at one of these pH values, but for accurate work, the analyses should be made at the pH optimum, as recommended by Weidenhagen.

4. HYDROLYSIS MEASUREMENTS

Two methods were used. In the first, a weighed quantity of emulsin was added to 10 ml of the substrate in undiluted buffer solution attemperated at 30° C. At appropriate times, 1- or 2-ml samples were removed with a pipette, added to 20 ml of copper sulfate-sodium citrate solution, and analyzed for reducing sugar by the modified Scales method.[37] A more accurate procedure is applied by adding 2 ml of enzyme solution to 8 ml of substrate solution, both attemperated at 30° C. The substrate concentration was always 2.375 g of sucrose or 1.013 g of inulin (anhydrous) in 50 ml of reaction mixture.[38]

[36] L. Wallerstein, Wallerstein Lab. Comm. No. 7, p. 10 (December 1939); U. S. Patents No. 1,919,675 and 1,919,676 (July 25, 1923).

[37] H. S. Isbell, W. W. Pigman, and H. F. Frush, J. Research NBS 24, 241 (1940) RP1282.

[38] In future work, the inulin concentration will be changed to 1.125 g of inulin in 50 ml, as suggested by Weidenhagen.

The temperatures were maintained at 30.0° ±0.3° C during the reaction period. Glass-stoppered test tubes provided satisfactory containers, and when the reaction required more than 8 hours, 2 ml of toluene was added to the reaction mixture. For the method of calculation, see section II, p. 162. The observed quantities of reducing sugar were corrected for the iodine consumption of enzyme and substrate blanks carried through a similar procedure and prepared as above, except that the substrate or enzyme was omitted.

A number of individuals and firms have been of great assistance in providing materials and advice in the present investigation. The writer expresses his appreciation for the cooperation of the following persons and firms: R. F. Jackson, E. McDonald, and C. F. Snyder, of the Polarimetry Section, National Bureau of Standards; Phillip Gray, representing the Wallerstein Laboratories, New York, N. Y.; S. Laufer, representing the Schwarz Laboratories, New York, N. Y.; W. N. Given and J. A. Shellenberger, representing the Röhm & Haas Co., Philadelphia, Pa.; C. W. Frey and W. R. Johnston, representing the Fleischmann Laboratories, New York, N. Y.; and J. J. Willaman, of the Eastern Regional Research Laboratory (United States Dept. of Agriculture).

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PERFORATED COVER PLATES FOR STEEL COLUMNS: COMPRESSIVE PROPERTIES OF PLATES HAVING CIRCULAR PERFORATIONS AND A WIDTH-TO-THICKNESS RATIO OF 53

By Ambrose H. Stang and Martin Greenspan

ABSTRACT

Tests were made to determine the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. Each test column was built up from one perforated plate and either two or four angles. Columns with unperforated plates were used as controls.

This paper gives the results of the tests on columns having plates of three different perforation spacings.

It was found that the perforated plates contributed to the strength and to the stiffness of the columns, and that the factor of stress concentration, due to the presence of the perforations, varied from 2.5 to 3.4 based on the gross area (2.2 to 2.8 based on the net area).

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I. INTRODUCTION

This paper is the fifth of a series dealing with the mechanical properties of perforated cover plates intended to be used as a substitute for lattice bars or batten plates in built-up box-type columns. An outline of the program, and results for plates having ovaloid perforations and widths of 15, 20, and 25.5 inches have been given in previous Research Papers [1, 2, 3, 4].[1]

In this paper are presented the test results for the *C1* series of plates. These plates were 20 in. wide by ⅜ in. thick, thus having a width-to-thickness ratio of 53. The perforated plates of this series had circular perforations 9 in. in diameter. The net-to-gross cross-sectional-area ratio was 0.55.

II. COVER-PLATE COLUMNS

1. GENERAL

The details of the *C1* plates and of the angles are shown in figure 1. The perforated *C1* plates were all of the same nominal dimensions as to length, width, thickness, and number and diameter of perforations but differed with regard to perforation spacing (i.e., the distance between centers of adjacent perforations). The perforation spacing was 21 inches for the *C1A* plates, 33 inches for the *C1B* plates, and 45 inches for the *C1C* plates. The *C1D* plates had the same nominal dimensions as the perforated *C1* plates but had no perforations. The *C1D* plates shown in figure 1 are the same plates as the *C3D* plates, the compressive properties of which are given in reference [4].

Each plate shown in figure 1 represents three like plates, designated (*0–1*), (*2–3*), and (*4–5*), and the angle shown represents many like angles which were used interchangeably with the plates to form the columns of which the cross sections are shown in the figure. The angles used with the plates to form the columns are given in table 1.

TABLE 1.—*Angles used for the C1 columns*

Column designation[1]	Angle designations
C1A(___) 2 angles	*C5D*(*4–5*), *C5G*(*0–1*).
C1A(___) 4 angles	*C5D*(*4–5*), *C5G*(*0–1*), *C5B*(*4–5*), *C5G*(*2–3*).
C1B(___) 2 angles	*C5B*(*4–5*), *C5G*(*2–3*).
C1B(___) 4 angles	*C5B*(*4–5*), *C5G*(*2–3*), *C5D*(*4–5*), *C5G*(*0–1*).
C1C(___) 2 angles	*C5H*(*0–1*), *C5H*(*2–3*).
C1C(___) 4 angles	*C5H*(*0–1*), *C5H*(*2–3*), *C5D*(*4–5*), *C5G*(*0–1*).
C1D(___) 2 angles	*C5A*(*0–1*), *C5E*(*4–5*).
C1D(___) 4 angles	*C5A*(*0–1*), *C5E*(*4–5*), *C5A*(*2–3*), *C5E*(*0–1*).

[1] The 3 columns represented by each of the above designations contained the same angles.

2. DIMENSIONS

The dimensions given in figure 1 are nominal. There were the usual commercial variations in the thicknesses and widths of the plates and angles. The variations in the dimensions of the perforations were considerably greater; for some plates the difference between the

[1] Figures in brackets indicate the literature references at the end of this paper.

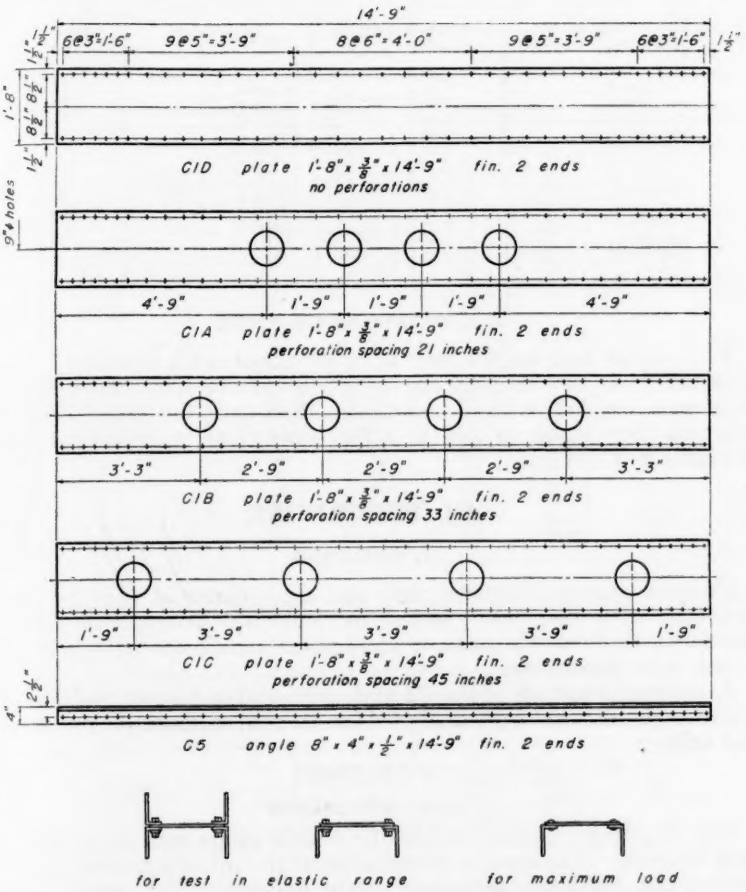

FIGURE 1.—*Plates and angles for the C1 columns*

minimum and maximum perforation diameter (width) was of the order of 0.3 in. The cross-sectional areas of the plates and angles, computed from the measured dimensions, are given in table 2.

TABLE 2.—*Cross-sectional areas of plates and angles for the C1 columns*

Plates			Angles	
Designation	Gross area	Net area	Designation	Area
	*in.*²	*in.*²		*in.*²
C1A(0-1)	7.54	4.12	*C5A(0-1)*	5.79
C1A(2-3)	7.54	4.20	*C5A(2-3)*	5.78
C1A(4-5)	7.63	4.22	*C5B(4-5)*	5.80
C1B(0-1)	7.53	4.16	*C5D(4-5)*	5.79
C1B(2-3)	7.47	4.14	*C5E(0-1)*	5.78
C1B(4-5)	7.54	4.18	*C5E(4-5)*	5.81
C1C(0-1)	7.74	4.28	*C5G(0-1)*	5.74
C1C(2-3)	7.65	4.21	*C5G(2-3)*	5.78
C1C(4-5)	7.61	4.20	*C5H(0-1)*	5.80
C1D(0-1)	7.67		*C5H(2-3)*	5.77
C1D(2-3)	7.62			
C1D(4-5)	7.57			

3. CONDITION OF ENDS

The plates and angles had been prepared with unusual care, so that the ends of the columns were reasonably flat. However, the ends were not flat in the sense that milled ends are flat. When the columns were stood on end on a flat steel plate, a definite tendency to teeter was observed.

III. PROCEDURE

1. COUPONS

Coupons representing the plate and angle material were cut in the direction of rolling and tested in tension. Young's modulus of elasticity, E; Poisson's ratio, ν; yield point, tensile strength, and elongation were determined.

A composite sample of the *C1* plate material and a composite sample of the angle material were analyzed for carbon, manganese, phosphorus and sulfur.

2. COLUMNS

(a) ELASTIC RANGE

The shortening under load in the elastic range was determined for each column. The strains in the edge of the middle perforation were determined for each perforated-plate column. The strains in the surfaces of the plate were determined for the middle bay of one of each group of three like perforated-plate columns having four angles. The distribution of stress in the middle bay of each of these columns was calculated from the strain data and the values of the elastic constants obtained from the coupon tests.

(b) MAXIMUM LOAD

One two-angle column of each group of three like two-angle columns was subjected to maximum-load test after the bolts had been replaced by rivets. Data to complete the stress-strain curves and data for stress-deflection curves were taken.

IV. RESULTS

1. COUPONS

The results of the tensile tests of the coupons are given in table 3.

TABLE 3.—*Results of tensile tests of coupons*

Coupon designation	Thickness	Young's modulus of elasticity, E	Poisson's ratio, ν	Yield point	Tensile strength	Elongation in 8 inches
PLATE COUPONS						
	Inches	*Kips/in.²*		*Kips/in.²*	*Kips/in.²*	*Percent*
C1A(1-2)	0.377	29,600	0.285	38.0	60.0	32.0
C1A(3-4)	.377	29,500	.280	39.4	60.1	32.8
C1B(1-2)	.377	29,500	.281	37.4	58.7	33.3
C1B(3-4)	.378	29,600	.280	38.1	58.7	30.6
C1C(1-2)	.385	29,600	.274	38.2	59.0	32.7
C1C(3-4)	.382	29,500	.278	37.5	58.4	34.1
C1D(1-2)	.382	29,400	.281	38.0	60.4	32.4
C1D(3-4)	.379	29,600	.276	38.6	60.5	32.7
ANGLE COUPONS						
C5A(1-2)	0.510	29,600	0.286	36.3	59.0	33.5
C5A(3-4)	.506	30,000	.290	35.6	58.7	33.5
C5B(1-2)	.506	29,700	.286	36.0	59.5	31.3
C5B(3-4)	.510	29,700	.278	35.9	58.7	35.8
C5D(1-2)	.500	29,800	.287	37.0	63.7	33.1
C5D(3-4)	.507	29,700	.288	36.9	64.5	33.0
C5E(1-2)	.508	29,700	.285	37.5	59.5	31.3
C5E(3-4)	.508	29,600	.281	36.0	59.1	33.1
C5G(1-2)	.509	30,100	.287	37.2	64.3	32.4
C5G(3-4)	.503	29,800	.285	37.0	69.2	31.7
C5H(1-2)	.512	29,400	.279	38.6	65.7	29.0
C5H(3-4)	.506	29,400	.282	38.0	65.7	31.5

The chemical composition of the coupon material is given in table 4.

TABLE 4.—*Chemical composition of coupon material*

Composite sample	Carbon	Manganese	Phosphorus	Sulfur
	Percent	*Percent*	*Percent*	*Percent*
Plates *C1*	0.17	0.56	0.008	0.03
Angles *C5*	.21	.56	.014	.03

2. COLUMNS

(a) MODULUS OF COLUMN AND EFFECTIVE AREA OF PLATE

The moduli, E', of the columns, and the effective-area factors, K, with respect to shortening under compressive load, for the plates, are given in table 5.[2]

[2] See pages 679 and 680 of reference [1].

TABLE 5.—*Moduli of columns, effective-area factors of plates, and maximum-stress ratios*

Plate designation	Number of angles	Based on gross area			Based on net area		
		Modulus, E'	Effective-area factor, K	Ratio, Maximum stress / P/A	Modulus, E'	Effective area factor, K	Ratio, Maximum stress / P/A
		Kips/in.^{2}			*Kips/in.*^{2}		
C1A(0–1)	2	25,000	0.63		30,400	1.14	
C1A(2–3)	2	25,100	.64		30,400	1.14	
C1A(4–5)	2	25,100	.64		30,600	1.16	
Avg		25,100	0.64	−2.77	30,500	1.15	−2.28
C1A(0–1)	4	26,600	0.62		29,900	1.14	
C1A(2–3)	4	26,800	.65		30,000	1.17	
C1A(4–5)	4	26,700	.65		30,000	1.17	
Avg		26,700	0.64	−2.50	30,000	1.16	−2.22
C1B(0–1)	2	26,000	0.71		31,500	1.29	
C1B(2–3)	2	26,000	.71		31,600	1.29	
C1B(4–5)	2	26,000	.71		31,500	1.28	
Avg		26,000	0.71	−3.24	31,500	1.29	−2.67
C1B(0–1)	4	27,200	0.71		30,500	1.29	
C1B(2–3)	4	27,200	.72		30,600	1.29	
C1B(4–5)	4	27,100	.70		30,500	1.26	
Avg		27,200	0.71	−2.91	30,500	1.28	−2.59
C1C(0–1)	2	26,700	0.78		32,500	1.40	
C1C(2–3)	2	26,700	.77		32,500	1.40	
C1C(4–5)	2	26,700	.77		32,400	1.40	
Avg		26,700	0.77	−3.43	32,500	1.40	−2.82
C1C(0–1)	4	27,600	0.78		31,100	1.40	
C1C(2–3)	4	27,500	.76		31,000	1.37	
C1C(4–5)	4	27,600	.76		31,000	1.38	
Avg		27,600	0.77	−3.06	31,000	1.38	−2.72
C1D(0–1)	2	29,400			29,400		
C1D(2–3)	2	29,300			29,300		
C1D(4–5)	2	29,200			29,200		
Avg		29,300	1.00		29,300	1.00	
C1D(0–1)	4	29,300			29,300		
C1D(2–3)	4	29,300			29,300		
C1D(4–5)	4	29,200			29,200		
Avg		29,300	1.00		29,300	1.00	

(b) STRESSES

(1) *On the edge of the perforation.*—The distribution of stress on the edge of the perforation is indicated in figures 2, 3, and 4. Each curve represents the average result for three like columns having the same perforation spacing.

The vertical axis of the graph in each figure is a development of one quadrant of the edge of the perforation.

In the stress ratios, $\sigma_{u,v}/(P/A_n)$, A_n is the net area of the column, and σ_u and σ_v are the maximum and the minimum principal stresses, respectively. The stress ratios based on gross area, $\sigma_{u,v}$ (P/A), may be obtained by multiplying $\sigma_{u,v}/(P/A_n)$ by 1.22 for the two-angle and 1.12 for the four-angle columns.

The maximum stress ratios are given in table 5.

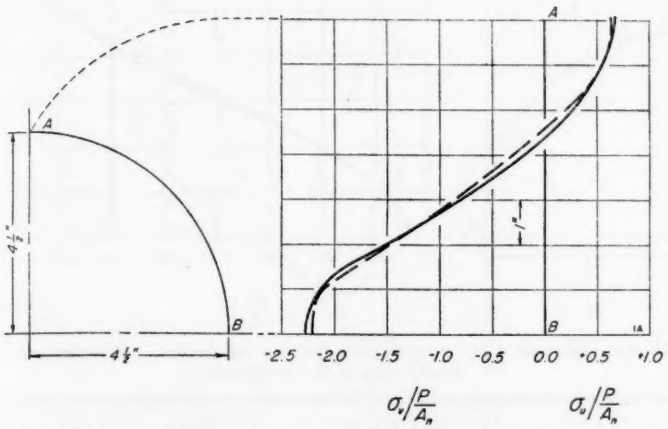

FIGURE 2.—*Columns C1A, perforation spacing 21 inches. Distribution of stress on the edge of the perforation.*

The solid line is for the two-angle column, and the dashed line for the four-angle column. Based on net area.

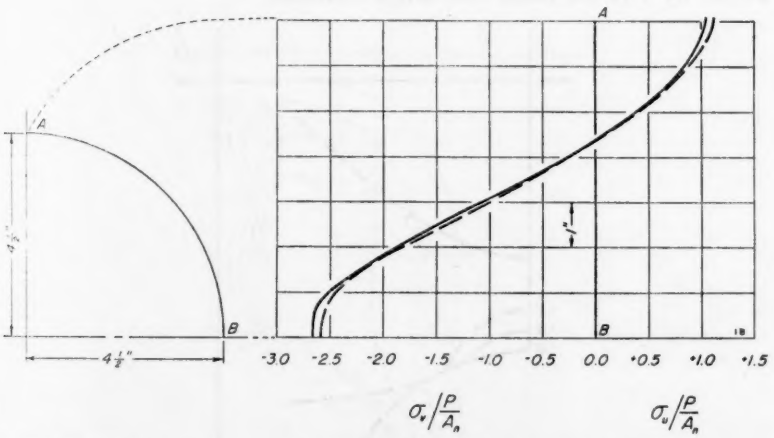

FIGURE 3.—*Columns C1B, perforation spacing 33 inches. Distribution of stress on the edge of the perforation.*

The solid line is for the two-angle column, and the dashed line for the four-angle column. Based on net area.

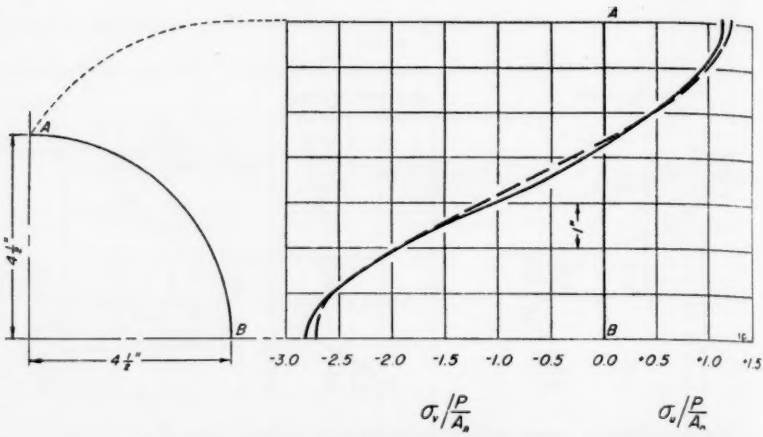

FIGURE 4.—*Columns C1C, perforation spacing 45 inches. Distribution of stress on the edge of the perforation.*

The solid line is for the two-angle column, and the dashed line for the four-angle column. Based on net area.

(2) *On the surfaces of the plate.*—The distributions of stress on the surfaces of the middle bay for the perforated plate columns having four angles are indicated in figures 5 to 16, inclusive. The stress ratios shown in these figures are based on net area. The stress ratios based on gross area may be obtained by multiplying the given values by 1.12 for these four-angle columns.

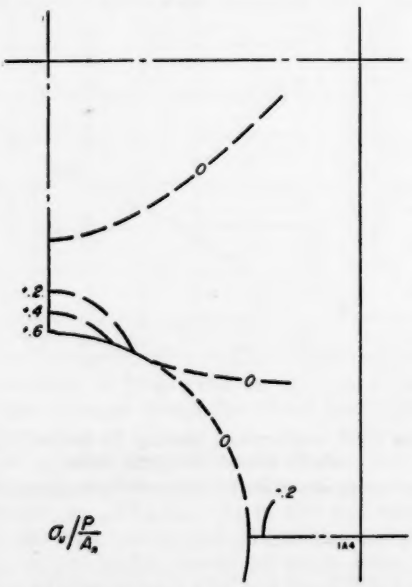

FIGURE 5.—*Column C1A (2–8) (four angles), perforation spacing 21 inches. Isogram of maximum principal stress.*

Based on net area.

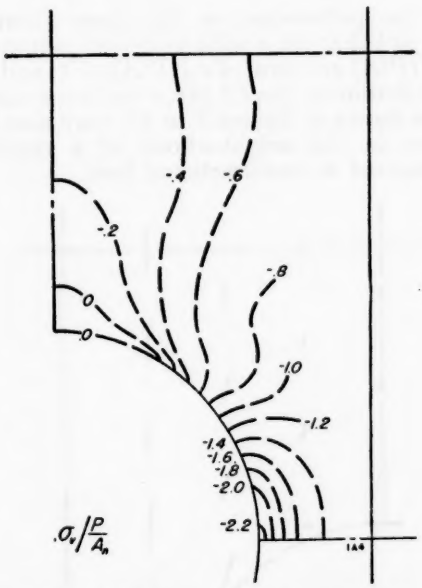

FIGURE 6.—*Column C1A (2–3) (four angles), perforation spacing 21 inches. Isogram of minimum principal stress.*

Based on net area.

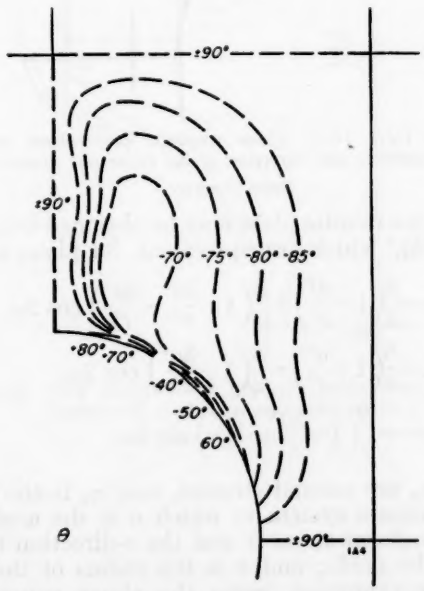

FIGURE 7.—*Column C1A (2–3) (four angles), perforation spacing 21 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

The effect of the perforation on the stress distribution may be judged from the fact that for a solid plate (no perforation) the values everywhere of $\sigma_u/(P/A)$ are zero; of $\sigma_v/(P/A)$, -1; and of θ, 90 degrees.

The stress distribution in the *C1* plates having a number of circular holes in a row, as shown in figures 5 to 16, may also be compared to stress distribution in the neighborhood of a circular hole in an infinite plate subjected to unidirectional load.

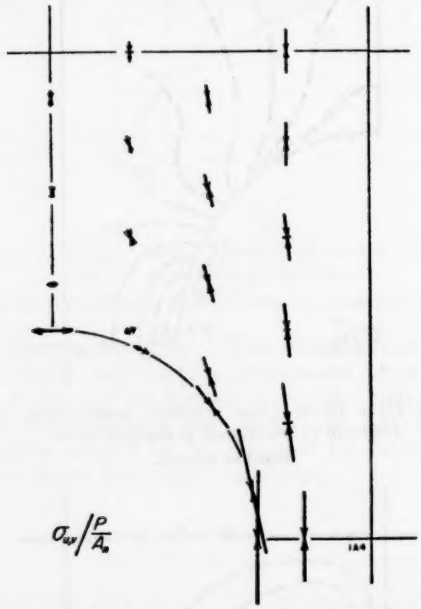

FIGURE 8.—*Column C1A (2–3) (four angles), perforation spacing 21 inches. Magnitude and direction of the principal stresses.*

Based on net area.

The stresses in the infinite plate may be obtained from the equations given by Kirsch [5],[3] which are equivalent, for plane stress, to

$$\sigma_r=\frac{S}{2}\left(1-\frac{a^2}{r^2}\right)+\frac{S}{2}\left(1+\frac{3a^4}{r^4}-\frac{4a^2}{r^2}\right)\cos 2\alpha,$$

$$\sigma_\alpha=\frac{S}{2}\left(1+\frac{a^2}{r^2}\right)-\frac{S}{2}\left(1+\frac{3a^4}{r^4}\right)\cos 2\alpha,$$

$$\tau_{r\alpha}=-\frac{S}{2}\left(1-\frac{3a^4}{r^4}+\frac{2a^2}{r^2}\right)\sin 2\alpha,$$

in which σ_r and σ_α are normal stresses, and $\tau_{r\alpha}$ is the shearing stress in the polar coordinate system in which α is the angle between the direction of the uniform stress S and the r-direction for which computations are to be made; and a is the radius of the circular hole. The stresses were evaluated, using the above equations and with $S=-1$, for a large number of points. From these values the magnitude and direction of the principal stresses for the points were found by the graphic method of O. Mohr,[4] and are shown in figures 17 to 20.

[3] Or see page 77 of reference [6].
[4] See page 17 of reference [6]

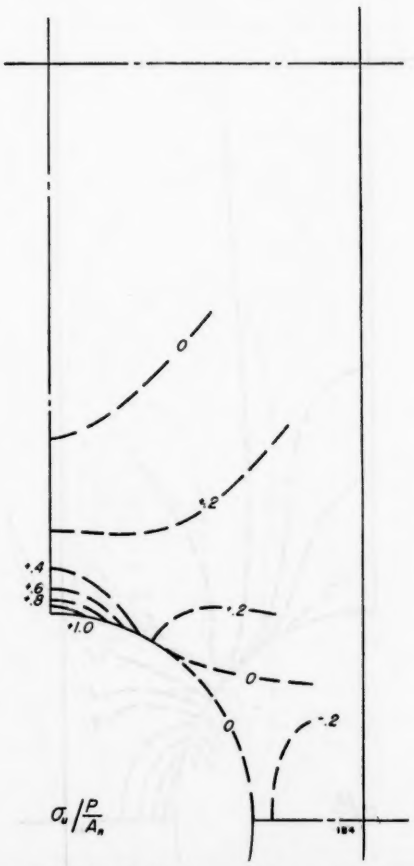

FIGURE 9.—*Column C1B (2–3) (four angles), perforation spacing 33 inches. Isogram of maximum principal stress.*

Based on net area.

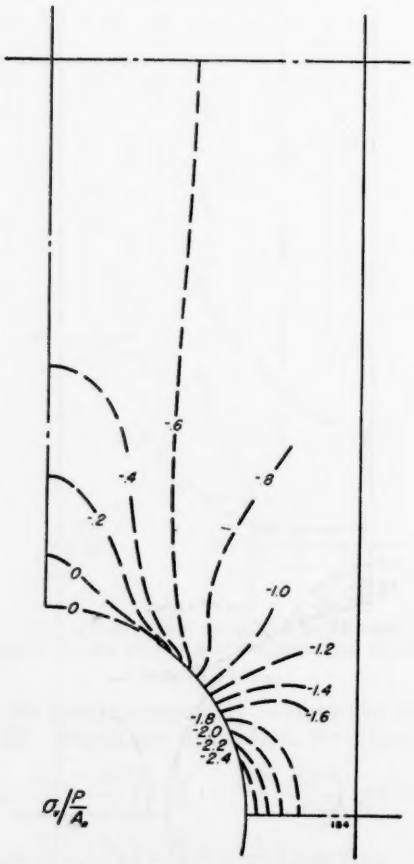

FIGURE 10.—*Column C1B (2–3) (four angles), perforation spacing 33 inches. Isogram of minimum principal stress.*

Based on net area.

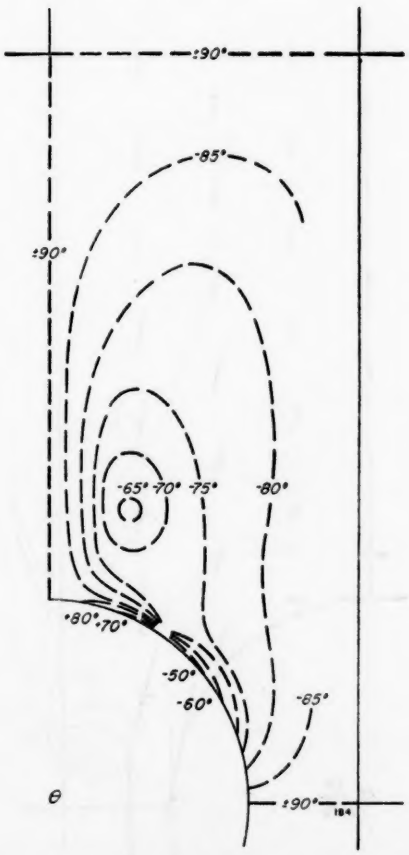

FIGURE 11.—*Column C1B (2–3) (four angles), perforation spacing 33 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

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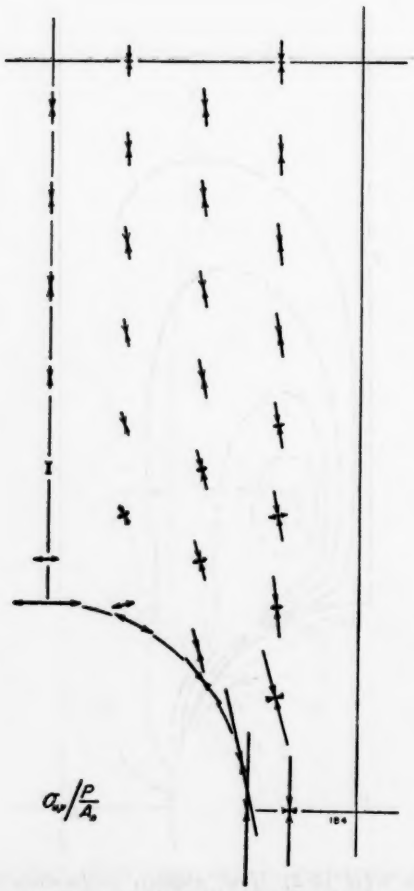

FIGURE 12.—*Column C1B (2–3) (four angles), perforation spacing 33 inches. Magnitude and direction of the principal stresses.*

Based on net area.

FIGURE 13.—*Column C1C (2–3) (four angles), perforation spacing 45 inches. Isogram of maximum principal stress.*

Based on net area.

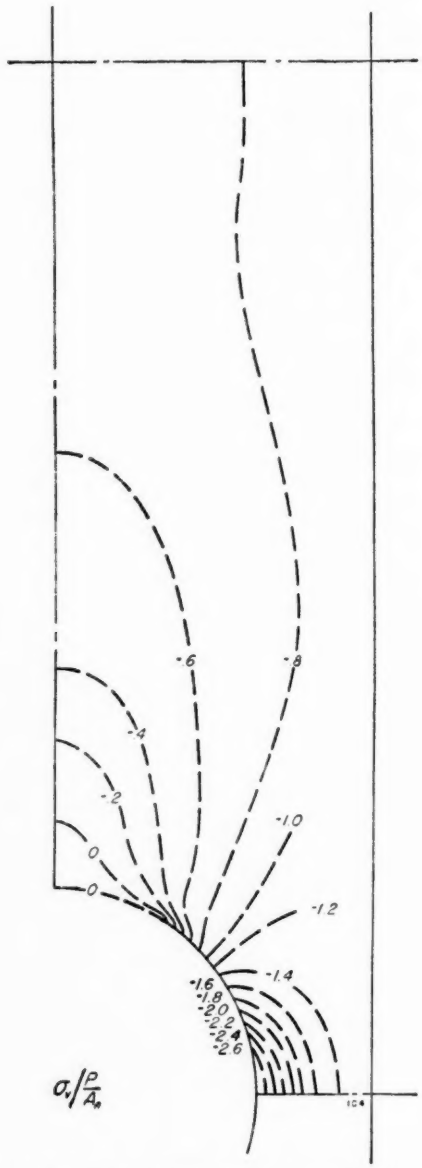

FIGURE 14.—*Column C1C (2–3) (four angles), perforation spacing 45 inches Isogram of minimum principal stress.*

Based on net area.

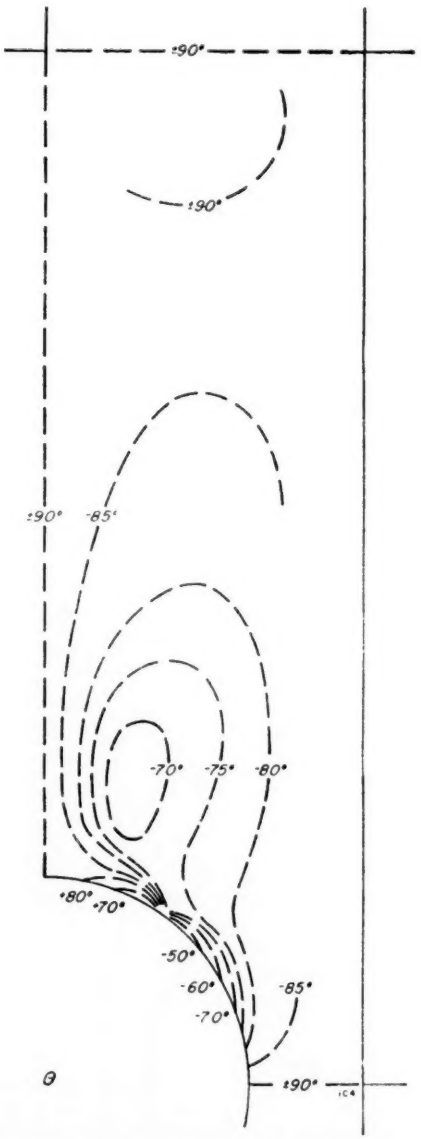

FIGURE 15.—*Column C1C (2–3) (four angles), perforation spacing 45 inches. Isoclinics.*

The angle θ is measured positive counterclockwise from the axis of the column to the direction of the maximum principal stress.

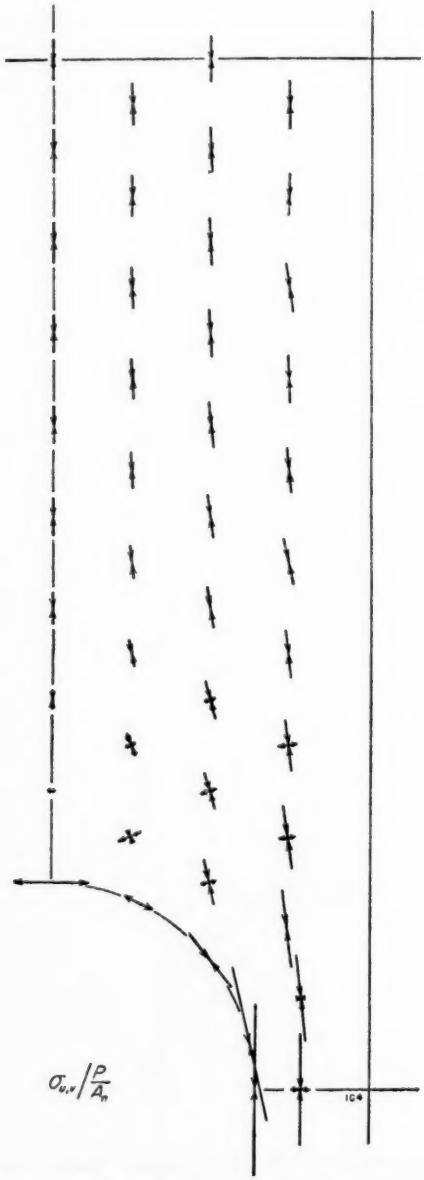

FIGURE 16.—*Column C1C (2–3) (four angles), perforation spacing 45 inches. Magnitude and direction of the principal stresses.*

Based on net area.

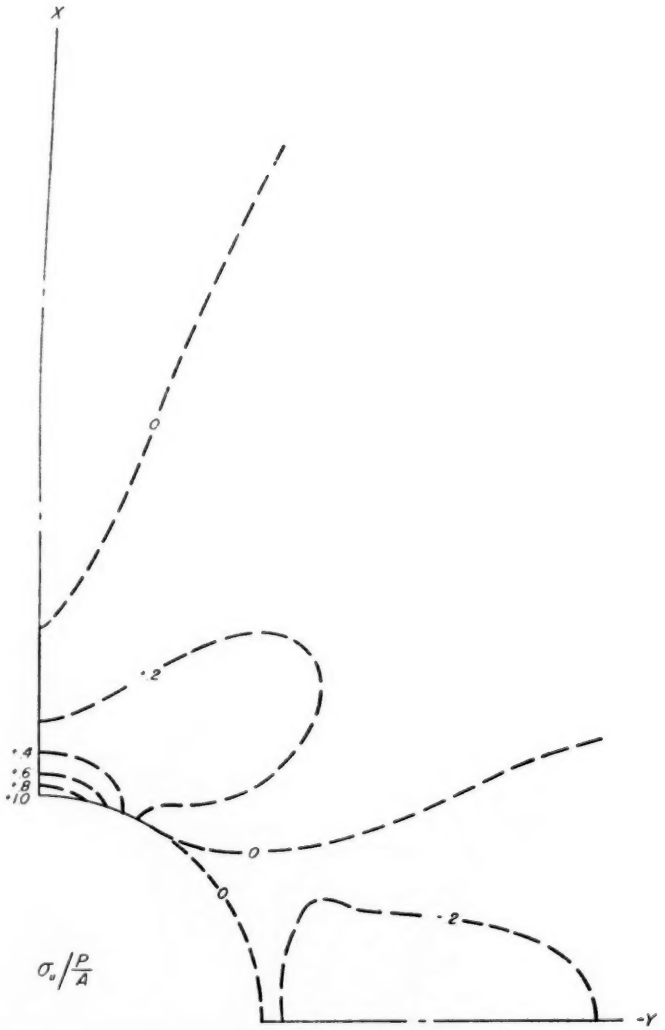

FIGURE 17.—*Isogram of maximum principal stress in the neighborhood of a circular hole in an infinite plate subjected to a uniform compression in the x-direction.*

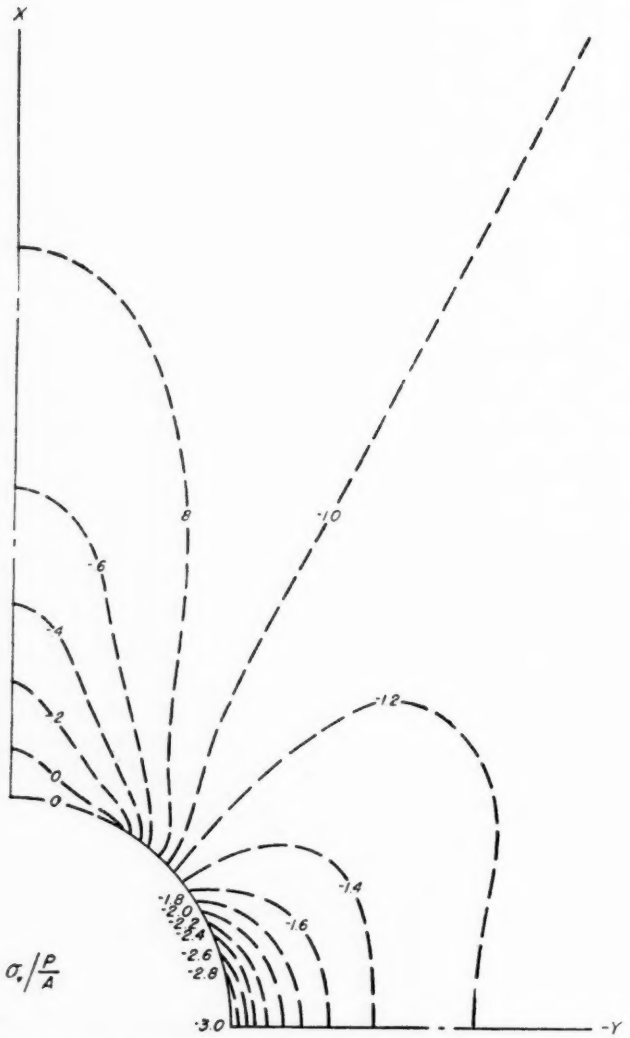

FIGURE 18.—*Isogram of minimum principal stress in the neighborhood of a circular hole in an infinite plate subjected to a uniform compression in the x-direction.*

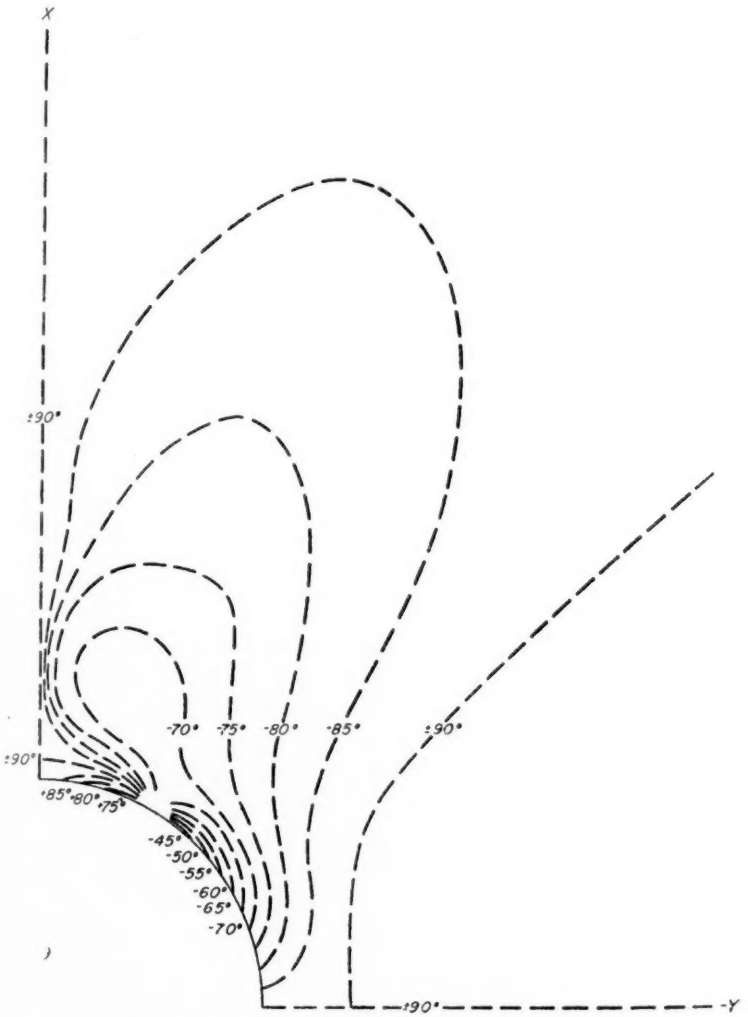

FIGURE 19.—*Isoclinics in the neighborhood of a circular hole in an infinite plate subjected to a uniform compression in the x-direction.*

The angle θ is measured positive counter clockwise from the x-direction to the direction of the maximum principal stress.

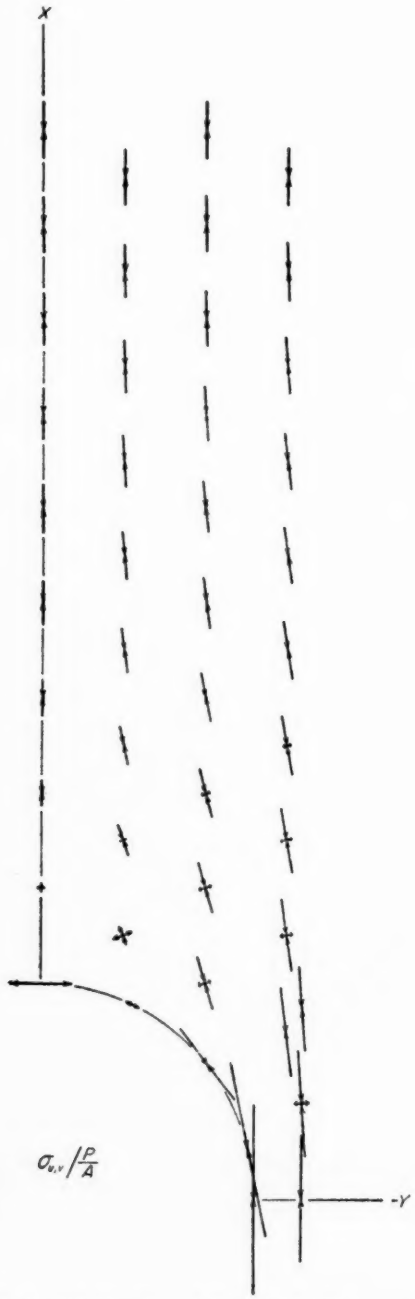

FIGURE 20.—*Magnitude and direction of the principal stresses in the neighborhood of a circular hole in an infinite plate subjected to a uniform compression in the x-direction.*

(c) MAXIMUM-LOAD TEST

(1) *Stress-strain graphs.*—The stress-strain graphs for the columns, based on net areas, are shown in figure 21.

The stresses on gross area may be obtained by multiplying the stresses on net area by 0.82.

(2) *Deflections.*—The stress-lateral-deflection graphs for the columns, based on net area, are shown in figure 22.

The stresses on gross area may be obtained by multiplying the stresses on net area by 0.82.

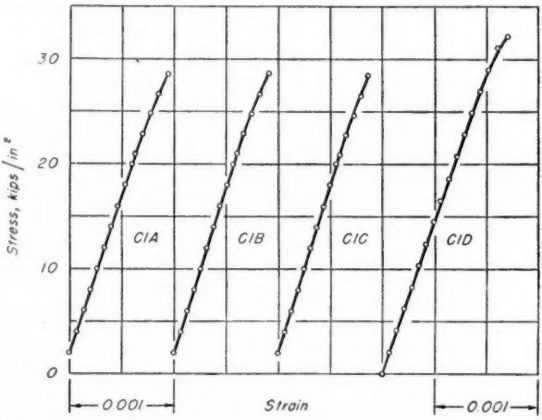

FIGURE 21.—*Columns C1-(two angles). Stress-strain graphs.*
Based on net area

(3) *Maximum load and effective area of plate.*—The maximum loads for the columns, the maximum average stress on the gross area and on the net area, and the effective-area factors of the plates with respect to compressive strength, *C*, are given in table 6.[5]

The perforated-plate columns, *C1A*, *C1B*, and *C1C* failed by primary buckling away from the plate side of the column, as would be expected from the consideration that, in the neighborhood of a per-

TABLE 6.—*Maximum loads for columns and effective-area factors for plates*

Column designation	*C1A*	*C1B*	*C1C*	*C1D*
Perforation spacing, *in.*	21	33	45	(a)
Area of angles, *in.*²	11.53	11.58	11.57	11.60
Gross area of plate, *in.*²	7.54	7.47	7.65	7.62
Net area of plate, *in.*²	4.20	4.14	4.21	7.62
Total area, gross, *in.*²	19.07	19.05	19.22	19.22
Total area, net, *in.*²	15.73	15.71	15.78	19.22
Maximum compressive load, *Kips*	541	540	561	624
Compressive stress on gross area at failure, *Kips/in.*²	28.4	28.3	29.2	32.5
Compressive stress on net area at failure, *Kips/in.*²	34.4	34.4	35.6	32.5
Effective-area factor of plate with respect to compressive strength, *C*:				
Based on gross area	0.68	0.68	0.74	1.00
Based on net area	1.22	1.22	1.35	----
Slenderness ratio	----	----	----	71
Column efficiency, *Percent*	----	----	----	87

[a] No perforation.

[5] See page 685 of reference [1].

foration, the gravity axis of the column is displaced away from the plate side. Local buckling of the outstanding legs of the angles of the columns occurred near the ends of the column.

The unperforated-plate column *C1D* started to deflect toward the plate side, as would be expected from the double-modulus theory, but

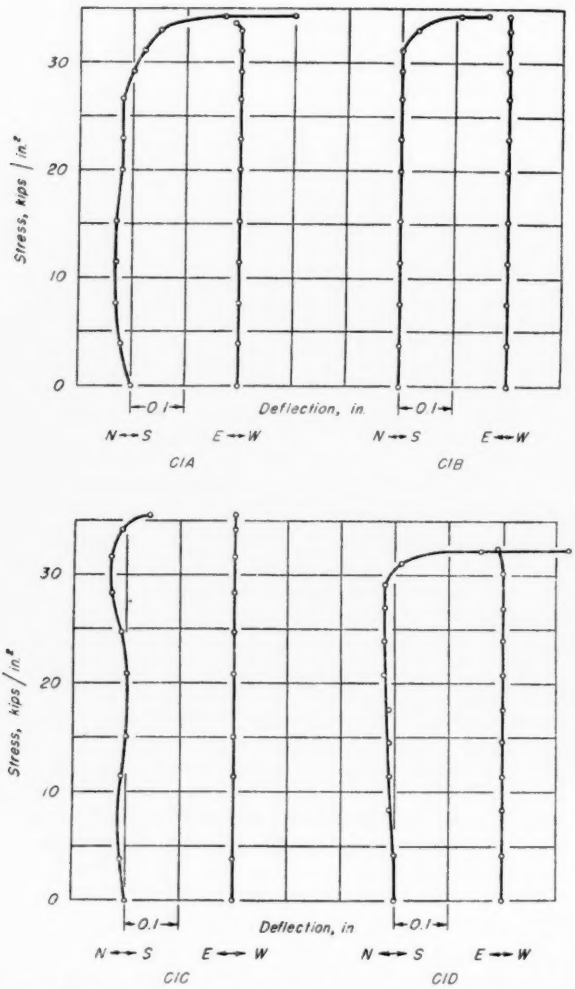

FIGURE 22.—*Columns C1-(two angles). Stress-deflection graphs.*

Based on net area. When the deflection is north, *N*, the bending stress is tensile on the plate side.

failed by secondary buckling of the plate at about one-third the height of the column from the base. The column efficiency of 87 percent, given in table 6, is the ratio of the average stress at failure to the weighted average yield point of the material determined from the tensile tests of the coupons. This value of column efficiency is lower than would be expected for a column having a slenderness ratio of

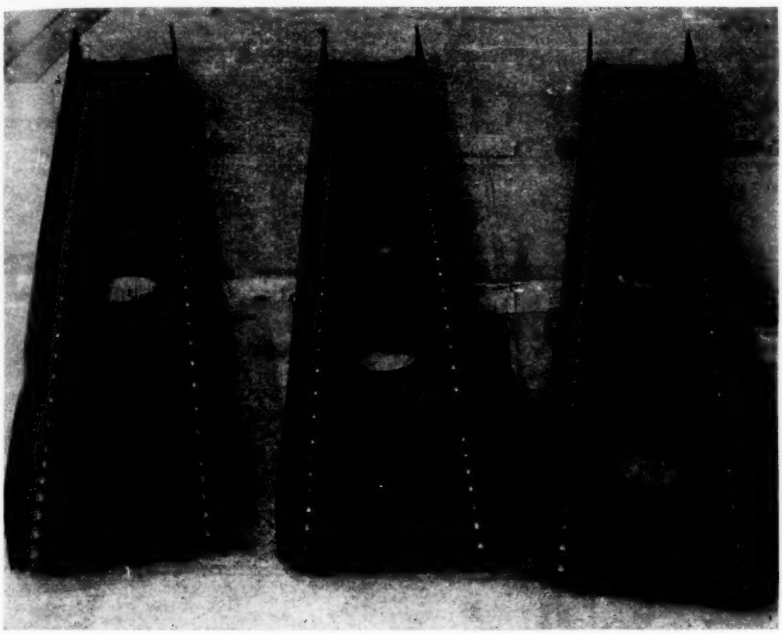

FIGURE 23.—*Columns C1—(two angles) after maximum load tests.*
From left to right the columns are *C1A*, *C1B*, and *C1C*.

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71 tested with flat ends. This low efficiency is due to the failure being at least partly by instability. The efficiency of column *C1D* is intermediate to the efficiencies of the two previously tested unperforated-plate columns; column *C2D* having a narrower cover plate and which failed largely as a whole, and column *C4D* having a wider cover plate and which failed largely by elastic instability.

The effective-area factors, *C*, of the perforated plates with respect to compressive strength are of course greater than they would have been if the unperforated-plate column had failed at a higher stress owing to primary buckling. It may be noted that the compressive stresses at failure are somewhat greater for these *C1* columns having circular perforations than for the *C3* columns of the same plate width but having ovaloid perforations.[6]

Figure 23 shows the columns after test.

V. SUMMARY

1. MODULUS

The effectiveness of the perforated plates in resisting shortening under compressive load was determined by a comparison of the modulus of a column containing the perforated plate with that of a similar column containing an unperforated plate. It was found that from 64 to 77 percent of the gross cross-sectional area of the plate, depending on the perforation spacing, was effective in resisting shortening under compressive load. The effective-area factors for the perforated plates were not affected by variation in the number of angles with which they were tested.

2. STRESS DISTRIBUTION

The stress distribution was determined on the edge of the perforation in the middle bay length of each perforated-plate column and on the middle bay of one of each group of three like columns having four angles. In every case the maximum stress was compressive and occurred on the edge of the perforation. The value of the maximum stress increased with increase of perforation spacing. For columns with the same perforation spacing, the maximum stress was higher for the two-angle than for the four-angle column for the same average stress on the gross area or on the net area.

The maximum stress varied from 2.5 to 3.4 times the average stress on the gross area, or 2.2 to 2.8 times the average stress on the net area. These values of stress concentrations for these circular perforations were greater than for any of the columns having ovaloid perforations.

3. STRENGTH

The effectiveness of the perforated plates with respect to strength was about the same as with respect to resistance to shortening and was little affected by change of perforation spacing. The compressive stresses at failure for the columns having circular perforations were somewhat greater than for columns having the same plate width but having ovaloid perforations.

[6] See page 36 of reference [4].

VI. REFERENCES

[1] Ambrose H. Stang and Martin Greenspan, *Perforated cover plates for steel columns: Program and test methods.* J. Research NBS **28,** 669 (1942) RP1473.

[2] Ambrose H. Stang and Martin Greenspan, *Perforated cover plates for steel columns: Compressive Properties of plates having ovaloid perforations and a width-to-thickness ratio of 40.* J. Research NBS **28,** 687 (1942) RP1474.

[3] Ambrose H. Stang and Martin Greenspan, *Perforated cover plates for steel columns: Compressive properties of plates having ovaloid perforations and a width-to-thickness ratio of 68.* J. Research NBS **29,** 279 (1942) RP1501.

[4] Ambrose H. Stang and Martin Greenspan, *Perforated cover plates for steel columns: Compressive properties of plates having ovaloid perforations and a width-to-thickness ratio of 53.* J. Research NBS **30,** 15 (1943) RP1514.

[5] G. Kirsch, *Die Theorie der Elastizität und die Bedürfnisse der Festigkeitslehre.* Z. Ver. deut. Ing. **42,** 797 (1898).

[6] S. Timoshenko, Theory of Elasticity (McGraw-Hill, Book Co. Inc., New York, N. Y. 1934.)

WASHINGTON, December 29, 1942.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1528

Part of Journal of Research of the National Bureau of Standards, Volume 30, March 1943

PART-WOOL BLANKETS FOR USE IN BARRACKS

By Herbert F. Schiefer, Louis R. Mizell,[1] and F. T. Mosedale[2]

ABSTRACT

The properties of 33 part-wool blankets of 8 constructions were measured, and the changes produced by 10 washings were observed. It is concluded that part-wool blankets should prove quite satisfactory for use in barracks in place of the all-wool army blanket, thereby effecting a substantial saving of wool, which might be needed for other military purposes.

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I. INTRODUCTION

The amount of wool produced in the United States is not sufficient to meet military and civilian needs, and it has been necessary to import considerable quantities of the fiber annually. In a critical situation, such as exists at present, in which the supply routes might be cut, the available supply might not be adequate to meet the essential military needs. The conservation of wool and the utilization of substitute fibers are therefore of considerable importance. The Office of the Quartermaster General of the United States Army has recognized the urgency of this problem by appointing a wool conservation committee to review Quartermaster Corps specifications for wool materials.

One possible means of accomplishing conservation of wool would be by replacing the regular all-wool army blanket with a part-wool blanket in barracks and other indoor quarters in the United States. In order to have data upon which to base specifications for part-wool blankets, 33 blankets of 8 constructions, containing either 50 percent of wool and 50 percent of cotton or 25 percent of wool and 75 percent of cotton, were subjected to analyses and tests. The results of these tests and of the tests of the regular all-wool army blanket are given in this paper.

[1] Research Associate at the National Bureau of Standards, representing the Textile Foundation.
[2] Representing United States Testing Co. Inc., Hoboken, N. J.

II. EXPERIMENTAL PROCEDURE

The testing procedure described in Research Paper RP1529 [1][3] and the equipment previously described [2, 3, 4] were used. The blankets were conditioned by exposure to air having a relative humidity of 65 percent and a temperature of 70° F, with a tolerance of ±2 percent in relative humidity and a temperature tolerance of ±2° F, and, except for thermal transmission, were tested under these conditions.

One blanket of each construction was washed in the military laundry at Fort Myer. The blankets were not renapped after washing. The properties of these blankets were measured after the first, fifth, and tenth washings.

Some of the blankets were tested at the U. S. Testing Co. The thermal-transmission tests were made in still air on equipment similar to that described by Cleveland [3] and also when the hood of the instrument was removed and a stream of air moving 6 miles per hour was directed across the sample. The blankets tested at the U. S. Testing Co. were washed once in a reversing wash wheel, in a 0.5-percent soap solution at 100° F for 10 minutes, followed by a 10-minute and a 1-minute rinsing also at 100° F. The samples were spread on a horizontal ventilated screen to dry.

The regular all-wool army blanket was washed in a commercial laundry and was not renapped.

III. RESULTS

The results of the tests are given in table 1. The following general conclusions may be drawn from them.

The unlaundered blankets containing 75 percent of cotton and 25 percent of wool were more compressible, thicker, more permeable to air, and had a greater insulating value than the unlaundered blankets containing 50 percent of cotton and 50 percent of wool and the regular all-wool army blanket. After 10 launderings the 2 series of blankets were essentially alike in these properties. The blankets increased in thickness, breaking strength, and weight per square yard with laundering and decreased in compressibility, air permeability, and thermal transmission. These changes resulted from the shrinkage of the blankets during washing. All the blankets were considerably felted after the tenth washing. This condition was indicated by the lowered compressibility and was quite apparent to the feel and in the general appearance of the blankets. In this respect the laundered blankets were more nearly like the all-wool army blanket than were the unlaundered blankets. The compressional resilience of the unlaundered blankets of 25-percent-wool content was lower than that of the 50-percent-wool blankets and very much lower than that of the regular all-wool army blanket. It increased with laundering, primarily because of the felting produced during laundering.

[3] Figures in brackets indicate the literature references at the end of this paper.

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TABLE 1.—*Results of tests on blankets*

Blanket number	Number of washings	Thickness at—		Compressibility	Compressional resilience	Thermal transmission Btu/(°F×hr×ft²)	Air permeability ft³/(min×ft²) at 0.5-in. H_2O pressure	Breaking strength (grab)		Weight		Size		Shrinkage	
		0.1 lb/in²	1.0 lb/in²					Warp	Filling			Length	Width	Length	Width
Blanket 137A. 50% of wool, 50% of cotton (approx.)															
		in.	*in.*	*in.³/lb*	*%*			*lb*	*lb*	*oz/yd²*	*lb*	*in.*	*in.*	*%*	*%*
1	0	[a] 0.168	[a] 0.112	[b] 0.25	[c] 39	[d] 0.90	84	50	77	15.6	4.26	84.1	67.2		
2	0	.167	.111	.25	39	.90	85			15.8	4.29	85.0	66.9		
2	1	.211	.136	.26	40					17.8	4.24	76.3	64.6	10	3
2	10	.202	.155	.16	44	.81	55	60	100	19.7	4.22	75.6	58.5	11	13
3	0	.170	.106	.26	31		77			15.5	4.25	84.9	67.0		
3	0	[e] *.190				*1.04*(1.20)		*54	*88		*4.25	*83.0	*67.0		
3	1	*.237				*0.98*(1.01)								*7	*3
Blanket 138A. 50% of wool, 50% of cotton (approx.)															
4	0	0.165	0.110	0.28	42	0.86	90	52	57	14.3	3.99	85.3	67.8		
5	0	.170	.106	.27	35	.86	90			14.4	4.03	85.2	57.9		
5	1	.203	.130	.27	38					16.3	3.95	76.8	65.3	10	4
5	10	.197	.145	.18	50	.84	57	58	77	18.0	3.96	74.9	60.9	12	10
6	0	.174	.111	.26	33		83			14.5	3.99	84.5	67.6		
6	0	*.210				*.94*(1.16)		*54	*61		*3.96	*83.0	*67.4		
6	1	*.217				*.99*(1.22)								*7	*1
Blanket 139A. 50% of wool, 50% of cotton (approx.)															
7	0	0.178	0.117	0.24	40	0.90	84	52	89	15.4	4.13	83.4	66.8		
8	0	.180	.117	.26	28	.90	85			15.2	4.19	85.2	66.8		
8	1	.195	.134	.24	35					17.6	4.20	77.4	63.8	9	4
8	10	.196	.148	.16	49	.83	55	64	96	19.7	4.12	75.0	57.9	12	13
9	0	.167	.109	.26	36		87			15.0	4.16	86.3	66.9		
9	0	*.195				*1.00*(1.17)		*54	*92		*4.17	*83.9	*66.6		
9	1	*.215				*1.02*(1.22)								*10	*3

See footnotes at end of table.

TABLE 1.—*Results of tests on blankets*—Continued

Blanket number	Number of washings	Thickness at—		Compressibility	Compressional resilience	Thermal transmission Btu/(°F×hr×ft²)	Air permeability ft³/(min×ft²) at 0.5-in. H_2O pressure	Breaking strength (grab)		Weight	Size		Shrinkage	
		0.1 lb/in²	1.0 lb/in²					Warp	Filling		Length	Width	Length	Width
Blanket 140A. 50% of wool, 50% of cotton (approx.)														
		in.	*in.*	*in.³/lb*	%			*lb*	*lb*	*oz/yd²*	*lb*	*in.*	*in.*	%	%
10	0	0.183	0.116	0.27	39	0.89	95	51	66	14.6	3.98	84.5	67.1		
11	0	.175	.112	.27	32	.89	90			14.7	4.05	84.6	67.2		
11	1	.215	.144	.25	36					17.1	4.07	76.3	64.7	10	4
11	10	.203	.146	.18	47	.82	59	59	83	18.7	4.01	74.0	60.0	13	11
12	9	.178	.114	.27	35		84			15.0	4.10	84.7	66.9		
12	0	*.205				*1.00*(1.19)		*54	*65		*4.10	*83.0	*66.8		
12	1	*.230				*1.04*(1.15)								*7	*1
Blanket 40050. 25% of wool, 75% of cotton (approx.)														
13	0	0.205	0.127	0.32	28	0.80	135	58	45	13.5	3.85	89.1	66.2		
14	0	.209	.131	.32	28	.80	131			13.7	3.87	88.9	65.6		
14	1	.242	.159	.26	32					15.9	3.70	78.0	61.8	12	6
14	10	.201	.144	.18	38	.79	75	59	53	17.4	3.61	74.3	58.0	16	12
15	0	.204	.127	.29	33		140			13.6	3.85	88.5	66.4		
15	0	*.222				*.99*(1.17)		*58	*49		*3.84	*87.3	*66.0		
15	1	*.250				*.97*(1.12)								*10	*4
16	0	.192	.127	.28	36		132			13.8	3.91	88.3	66.4		
17	0	.215	.126	.31	28		140			13.1	3.76	89.4	66.3		
18	0	.211	.127	.33	22		144			14.1	3.91	89.3	66.5		
Blanket 40051. 25% of wool, 75% of cotton (approx.)														
19	0	0.203	0.134	0.30	34	0.80	133	61	47	14.4	4.00	87.9	66.2		
20	0	.212	.135	.30	23	.80	137			14.1	3.99	88.8	66.2		
20	1	.239	.162	.25	28					17.1	3.94	77.1	62.0	13	6
20	10	.199	.150	.16	37	.77	74	60	61	17.9	3.72	75.0	57.3	16	14
21	0	.223	.136	.29	26		137			14.1	3.98	88.3	66.2		
21	0	*.215				*1.02*(1.20)		*64	*59		*3.95	*87.4	*66.3		
21	1	*.255				*0.95*(1.23)								*10	*6
22	0	.218	.133	.29	24		129			14.2	4.00	88.2	66.3		
23	0	.200	.123	.30	27		137			14.1	4.00	88.1	66.9		
24	0	.202	.126	.30	22		136			14.0	3.97	88.8	66.1		

Blanket 40052. 25% of wool, 75% of cotton (approx.)

25	0	0.197	0.127	0.30	35	0.85	119	56	47	14.1	3.98	88.3	66.2		
26	0	.224	.137	.31	27	.85	111			14.1	3.99	88.1	66.3		
26	1	.237	.161	.25	31					16.4	3.88	78.5	62.4	11	6
26	10	.189	.143	.17	38	.80	67	53	60	17.2	3.82	77.3	59.4	12	10
27	0	.215	.138	.29	22		115			14.4	4.04	88.8	66.3		
27	0	*.235				*.98*(1.17)		*60	*54		*4.03	*87.0	*66.1		
27	1	*.258				*.99*(1.20)								*10	*5
28	0	.217	.136	.30	23		117			14.3	4.03	88.1	66.2		

Blanket 40053. 25% of wool, 75% of cotton (approx.)

29	0	0.213	0.133	0.31	29	0.85	133	45	44	13.5	3.87	88.7	67.2		
30	0	.229	.137	.31	28	.84	140			13.6	3.81	88.4	66.8		
30	1	.249	.171	.26	28					15.6	3.68	78.0	62.7	12	6
30	10	.210	.155	.17	36	.81	80	50	54	16.9	3.54	75.0	58.0	15	13
31	0	.217	.135	.30	30		132			13.5	3.88	88.5	67.2		
31	0	*.225				*.96*(1.18)		*50	*47		*3.87	*87.6	*67.4		
31	1	*.245				*1.00*(1.10)								*5	*4
32	0	.225	.146	.28	21		137			13.6	3.89	88.3	67.2		
33	0	.209	.132	.32	29		135			13.4	3.86	88.7	67.3		

Regular army blanket. 100 percent of wool

34	0	0.152	0.098	0.23	48	0.96	101	63	59	14.3					
34	1	.163	.110	.23	49	1.00	69	71	60	15.8				4	6
34	10	.160	.111	.22	54	.91	75	70	62	16.5				8	6

[a] A presser foot 1 inch in diameter was used, except in those cases where the values are marked with an asterisk, which were obtained with a pressure foot 3.5 inches in diameter and a pressure of 0.0125 lb/in.^{2} at the U. S. Testing Co.

[b] A high value for compressibility indicates a greater amount of napping and less felting.

[c] A high value for compressional resilience indicates greater ability of the blanket to come back to its initial state upon release of a compressive load.

[d] A low value for thermal transmission indicates a high insulating value. The values within the parentheses were obtained with the upper surface of the specimen exposed to air moving at a speed of 6 miles per hour.

* The values marked with an asterisk in the table were determined by the U. S. Testing Co.

Tests for color fastness to light and washing made at the U. S. Testing Co., showed no appreciable difference between these blankets. All the blankets showed good color fastness when exposed for 50 hours in a Fade-Ometer and when washed for 30 minutes in a suds of 0.5-percent-neutral soap at 100° F. Wear tests made on the U. S. Testing Co. abrasion machine showed no significant difference in the wear resistance of these blankets.

The shrinkages of the part-wool blankets were nearly twice the shrinkage of the regular all-wool army blanket. To compensate for the rather large shrinkages of these blankets, the original dimensions should be increased.

The results of the tests indicate that the blankets tested compare quite favorably with the regular all-wool army blanket and therefore should prove satisfactory for use in barracks, provided allowance is made for shrinkage. The 75-percent-cotton and 25-percent-wool blankets probably will shed fibers more readily during use, which may be somewhat objectionable. Their greater thickness, compressibility, and lower thermal transmission commend them, and greater saving in wool would, of course, result from their use.

IV. REFERENCES

[1] H. F. Schiefer, *Advantages of a blanket-and-sheet combination for outdoor use*, J. Research NBS **30**, 209 (1943) RP1529.

[2] H. F. Schiefer, *The compressometer—An instrument for evaluating the thickness, compressibility, and compressional resilience of textiles and similar materials*, NBS J. Research **10**, 705 (1933) RP561.

[3] R. S. Cleveland, *An improved apparatus for measuring the thermal transmission of textiles*, J. Research NBS **19**, 675 (1937) RP1055.

[4] H. F. Schiefer and P. M. Boyland, *Improved instrument for measuring the air permeability of fabrics*, J. Research NBS **28**, 637 (1942) RP1471.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1529

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ADVANTAGES OF A BLANKET-AND-SHEET COMBINATION FOR OUTDOOR USE

By Herbert F. Schiefer

ABSTRACT

Blankets varying greatly in air permeability were tested alone and in combination with one and with two sheets for air permeability and thermal transmission. The air permeability of the sheets was low in comparison with that of the blankets. The results show the effect of moving air on the thermal transmission of the blankets and of the blankets between two sheets. The effect of laundering on the weight, thickness, compressibility, compressional resilience, breaking strength, air permeability, and thermal transmission of the blankets is also reported.

It is concluded that for outdoor use, where protection against the wind and rain or snow is important, as in an open lifeboat at sea, a combination of a blanket and sheet or wind-resistant cloth would afford far more protection than a blanket alone.

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I. INTRODUCTION

Blankets are used by the armed forces under many different conditions, and are relied upon considerably to afford the soldier warmth and comfort and to protect his health. A blanket which keeps a person warm when he is shielded from the elements may not give sufficient protection to one exposed directly to the wind and snow or rain. This is particularly true in an open lifeboat, in which blankets are a part of the regular provisions.

Although blankets are commonly used in conjunction with sheets in homes, hospitals, and barracks, the possibilities of a sheet-blanket combination for outdoor use, where protection from wind and rain or snow, as well as cold, is important, apparently has not received very serious consideration.

An extensive study of the properties of blankets, recently completed at the National Bureau of Standards, included tests of combinations of blankets and sheets. The results of these tests are presented in this paper.

II. MATERIALS TESTED

Five all-wool blankets that differed very greatly in air permeability were selected for systematic testing in combination with one and two sheets. Their properties were measured when new and also after 1, 5,

and 10 washings. Twenty-two additional blankets and combinations of these blankets with one and two sheets were measured for thermal transmission only. The sheets used in the combinations conformed to Federal Specification CCC–S–271,[1] which requires a minimum of 74 threads per inch in the warp and 66 in the filling, a minimum weight of 4.6 oz/yd^2, and a minimum breaking strength (grab method) of 70 pounds in the warp and filling directions.

III. TESTING PROCEDURE

The weight, thickness, compressibility, compressional resilience, breaking strength, air permeability, and thermal transmission of the blankets, when new and after 1, 5, and 10 washings, were measured. The air permeability of combinations of one and two sheets with the five all-wool blankets, when new and after washing, was measured. The thermal transmission of these five blankets when new and the combinations with one and two sheets were measured in still air and also in air moving 15 miles per hour.

The blankets were conditioned by exposure to air having a relative humidity of 65 percent and a temperature of 70° F, with a tolerance of ±2 percent in relative humidity and a temperature tolerance of ±2° F and, except for thermal transmission, were tested under these conditions.

The thickness, compressibility, and compressional resilience were measured with the compressometer.[2] The thickness measurements were made at increasing pressures, namely 0.10, 0.20, 0.35, 0.50, 0.75, 1.00, 1.50, and 2.00 lb/in.,[2] and again at these pressures but in reversed order. These measurements were repeated at five random positions. The average of the five values at each pressure was taken as the thickness of the blanket at that pressure. The compressibility [3] was computed by dividing the decrease in thickness when the pressure was increased from 0.50 to 1.50 lb/in.[2] by the thickness at a pressure of 1.00 lb/in.[2] A high value indicates a greater amount of napping and less felting. The compressional resilience was taken to be the work recovered when the pressure was decreased from 2.00 to 0.10 lb/in.[2], expressed as a percentage of the work expended when the pressure was increased from 0.10 to 2.00 lb/in.[2] A high value indicates greater ability of the blanket to return to its initial state upon release of a compressive load.

The thermal transmission was measured with the equipment described by Cleveland.[4] It consists essentially of a square metal plate, in a horizontal position, provided with heating elements and thermostats for heating it to a predetermined temperature, approximately 113° F, and maintaining it at this temperature. Loss of heat from the plate in all directions except upward through the specimen is prevented by guard elements heated to the same temperature as the plate. A metal hood is provided to eliminate the influence of air

[1] Federal Specification for Sheeting: Cotton, Bleached, Wide, Superintendent of Documents, Washington, D. C. Price 5 cents, January 6, 1931.

[2] Herbert F. Schiefer, *The compressometer—An instrument for evaluating the thickness, compressibility, and compressional resilience of textiles and similar materials*, BS J. Research **10**, 705 (1933) RP561.

[3] "Compressibility" is defined as the decrease in thickness in unit thickness per unit pressure, dh/hdP, where h is the thickness at a pressure of P, and dh is the decrease in thickness corresponding to an increase in pressure of dP. In this paper P and dP are taken as equal to 1 lb/in.[2]

[4] Richard S. Cleveland, *An improved apparatus for measuring the thermal transmission of textiles*, NBS J. Research **19**, 675 (1937) RP1055.

currents. The plate and the inside and outside of this hood are painted with carbon-black lacquer to produce a surface having an emissivity between 0.95 and 1.00. Means are provided for determining the amount of heat supplied to the plate, the temperature of the top of the hood, the temperature difference between the plate and the top of the hood, and the temperature difference between the plate and the guard elements. The amount of heat supplied to the plate per unit of time divided by the difference in temperature between the plate and the hood and by the area of the plate is taken as the thermal transmission of the blanket in still air.

Some of the blankets were tested on similar equipment at the U. S. Testing Co.[5] in still air and also when the hood was removed and a stream of air moving 15 miles per hour was directed across the sample.

The air permeability was measured with the instrument described by Schiefer and Boyland.[6] It consists essentially of a suction fan for drawing conditioned air through the blanket, a circular orifice 2.75 in. in diameter over which the blanket is clamped, a means of measuring the pressure drop across the blanket, and provision for measuring the volume of air flowing through the blanket. The air permeability of the blanket is the volume of air passing through 1 sq. ft. of fabric per minute when the pressure drop across the blanket is equal to 0.5 in. of water.

The breaking strength (grab method) and the weight of the blankets were measured in accordance with the methods of Federal Specification CCC–T–191a.[7]

The blankets were washed 10 times in a commercial laundry. They were not renapped after washing. Marks were sewed on the blanket, and the distances between them were measured before and after laundering. The shrinkage of each blanket was computed from these dimensions.

IV. RESULTS

The results of the tests are given in table 1. The following conclusions may be drawn from them.

The air permeability of the combination of a blanket and one or two sheets was found to be practically independent of the air permeability of the blanket and was equal to or slightly less than that of the sheet or sheets alone.

The thermal transmission in still air decreased considerably when one or two sheets were used in combination with a blanket. The average decrease in thermal transmission for all the blankets tested was 7 percent when the sheet was used under the blanket, 15 percent when the sheet was used over the blanket, and 19 percent when the blanket was used between two sheets. The results obtained at the U. S. Testing Co. did not show as marked a decrease when the tests were made in still air. However, the thermal transmission of the blankets between two sheets, tested in air moving 15 miles per hour, decreased an average of 60 percent, and the value for the most permeable blanket was less than that of the least permeable and heaviest blanket. The thermal transmission of the blankets when tested alone in moving

[5] The assistance of the U. S. Testing Co., Inc., Hoboken, N. J., is gratefully acknowledged.

[6] Herbert F. Schiefer and Paul M. Boyland, *Improved instrument for measuring the air permeability of fabrics*, NBS J. Research **28** 637 (1942) RP1471.

[7] Federal Specification for Textiles; General Specifications, Test Methods, April 23, 1937. Superintendent of Documents, Washington, D. C. Price 5 cents.

TABLE 1.—*Results of tests on 5 all-wool blankets*

Blanket	Number of washings	Weight	Thickness at pressure of—		Compressibility [a]	Compressional resilience [b]	Breaking strength (grab)		Shrinkage	
			0.1 lb/in.²	1.0 lb/in.²			Warp	Filling	Warp	Filling
		oz/yd²	*in.*	*in.*	*in.²/lb*	%	*lb*	*lb*	%	%
A	0	12.6	0.231	0.122	0.34	47	37	39		
	1	13.9	.238	.147	.29	49	52	53	6	0
	10	13.8	.265	.155	.32	46	53	61	12	0
B	0	9.8	.193	.102	.40	50	34	13		
	1	10.6	.183	.112	.31	51	43	27	5	3
	10	11.3	.173	.107	.28	51	38	30	7	5
C	0	14.9	.230	.128	.37	50	56	36		
	1	15.4	.261	.150	.38	50	59	35	3	1
	10	17.3	.265	.173	.29	49	66	43	8	3
D	0	14.7	.233	.157	.28	50	56	48		
	1	16.1	.216	.167	.18	52	74	60	4	6
	10	18.0	.215	.163	.18	53	79	75	10	9
E	0	16.5	.151	.100	.22	48	68	71		
	1	17.5	.171	.121	.23	54	68	70	6	3
	10	18.1	.167	.119	.19	52	68	77	8	3

Blanket	Air permeability [a] ft³/(min × ft²) at 0.5-in. H_2O pressure			Thermal transmission, Btu/(°F × hr × ft²) [d]							
	Blanket alone	Sheet 1 under blanket	Sheet 2 over and Sheet 1 under blanket	Blanket alone	Sheet under blanket	Sheet over blanket	Sheet over and under blanket	Blanket alone		Blanket between two sheets	
								Still air	Moving air [e]	Still air	Moving air [e]
A	498	19	11	0.74	0.71	0.62	0.61	*0.80	*1.74	*0.77	*1.03
	427	19	11	.74							
	435	19	11	.72							
B	326	18	10	.82			.66	*.86	*1.95	*.81	*1.13
	257	18	10	.86							
	242	19	10	.81							
C	212	18	10	.78	.73		.62	*.78	*1.91	*.76	*1.06
	192	18	10	.74							
	183	19	11	.73							
D	127	17	10	.82	.76		.66	*.79	*1.38	*.74	*1.00
	99	16	10	.82							
	92	16	10	.78							
E	45	13	8	.95	.88	.79	.77	*1.00	*1.64	*.88	*1.20
	41	12	8	.95							
	41	12	8	.89							

[a] A high value for compressibility indicates a greater amount of napping and less felting.

[b] A high value for compressional resilience indicates greater ability of the blanket to return to its initial state upon release of a compressive load.

[c] The values for sheet 1, sheet 2, and the combination of sheet 1 and 2 were 19, 23, and 10, respectively.

[d] A low value for the thermal transmission indicates a high insulating value. The value for the sheet alone was 1.36. The asterisk indicates that the value was obtained by the U. S. Testing Co., Inc.

[e] The speed was 15 miles per hour.

air was over 100 percent greater than when they were tested in still air. The thermal transmission of the blankets when tested between two sheets in moving air was only 37 percent greater than when the combination was tested in still air.

The thermal transmission values obtained at the United States Testing Co. are consistently higher than those obtained at the National Bureau of Standards. The higher values probably result because the heat loss from the sides of the hood, which are continually exposed to moving air, is greater than that which is lost when the hood is in still air. A slight leakage of air into the hood may also have contributed to the observed differences.

The weight, thickness, and breaking strength of the blankets increased with the number of washings, and the compressibility and air permeability decreased. These changes are attributed to the shrinkages of the blankets during laundering. The compressional resilience of these blankets and the air permeability of the combination of a blanket and one or two sheets were not affected significantly by the number of washings.

For outdoor use where protection against the wind and other elements is important, as in an open lifeboat at sea, a combination of blanket and sheet would afford far more protection than the blanket alone. Such a combination would permit the use of a medium-weight blanket, and the blanket need not be greatly felted. The combination would not only be more flexible and easier to wrap around the body, but it would also be much warmer in a strong breeze. The sheet would provide additional strength, 60 lb or more per inch of width, and it could be made water repellent. This combination would effect a substantial saving in wool, which might be important in the event that the supply of wool should become a critical problem.

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COMPOSITION AND PHYSICAL PROPERTIES OF AQUEOUS EXTRACTS FROM PORTLAND CEMENT CLINKER PASTES CONTAINING ADDED MATERIALS

By George L. Kalousek, C. H. Jumper, and J. J. Tregoning

ABSTRACT

Mixtures of 12 commercial portland cement clinkers and water were filtered at 7 minutes and at 2 hours after mixing, and the chemical composition, pH, conductivity, surface tension, and density of the extracts were determined. The effects on the composition and physical properties of the extracts, produced by the addition of small amounts of various materials to the pastes, were studied in parallel experiments. The added materials included gypsum, which was used in preparing the cements from the clinkers, calcium chloride, calcium acetate, fluosilicic acid, sucrose, T D A, tannic acid, and triethanolamine.

In the majority of the extracts, soda and potash were present in greater amounts than any of the other dissolved oxides. Relatively high concentrations of sulfate occurred in the extracts of the clinkers that contained the larger amounts of potash. The lime concentration and basicity of the extracts were largely determined by the amounts of alkali oxides present. The concentration of silica corresponded approximately to the reported solubility of silica in lime solutions. Low concentrations of oxides of the R_2O_3 group were found except in extracts from pastes containing the added organic materials.

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I. INTRODUCTION

A comprehensive series of investigations was undertaken at this Bureau to provide much needed information on the character of the liquid phase following the gaging of portland cements with water, both in the absence and in the presence of various materials that have been suggested for the control of the reactions of hydration. The important variables in the study included:

1. Compositions of the cement clinkers.
2. Presence of additive materials.
3. Time of the reactions.

The first report on the series [1] [1] presented observed relations between the potash and the sulfur trioxide contents of the clinkers and of the extracts, leading to the belief that potash is present in many clinkers partly as potassium sulfate. The present (second) report gives information on the effects of clinker composition, character of material added, and time of reaction on the composition, surface tension, density, hydrogen-ion concentration (pH), and specific conductivity of the extracts. The third report [2] includes data on the effects of these same variables on the heats of hydration of the clinkers, the flows and strengths of specimens fabricated from the pastes after removal of the extracts, and the results of certain miscellaneous tests on the clinkers.

Because the amounts of extractable soda and potash in cements and their possible effects on the properties of cement products have been much discussed subjects for many years, the clinkers used in this study were chosen to give a large range in soda and potash contents. The materials added to the clinkers were gypsum, calcium chloride, calcium acetate, fluosilicic acid, sucrose, T D A, tannic acid, and triethanolamine. These substances are referred to as "added materials" or "addition agents" rather than as "admixtures."

II. MATERIALS

1. CLINKERS

The chemical analyses and computed compound compositions of the clinkers [3] are presented in table 1. It is to be noted that the soda content varied from 0.02 to 0.87 percent and the potash content from 0.05 to 1.32 percent.

The clinkers represented standard (Nos. 1, 2, 3, 4, 6, 7, 11, and 12), moderate-heat-of-hardening (Nos. 5, 8, and 9), and sulfate-resisting (No. 10) types. No. 2, a white clinker (low Fe_2O_3), had a high ignition loss and high free-lime content. Nos. 4 and 5 were the products of one manufacturer, and Nos. 7 and 8 were the products of another manufacturer. All the remaining clinkers were obtained from different plants.

The clinkers, in 600-lb lots, were ground to the finenesses reported in table 1, as determined by Wagner's method [4]. The experiments on a given clinker were nearly completed before the next clinker was ground.

[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Chemical analyses, potential compound compositions and finenesses of ground clinkers*

Clinker	Chemical composition, percent								Loss on ignition	Insoluble	Free CaO	Potential compound composition,[a] percent				Fineness
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3				$3CaO.SiO_2$	$2CaO.SiO_2$	$3CaO.Al_2O_3$	$4CaO.Al_2O_3Fe_2O_3$	
																cm²/g
1	23.9	5.6	3.4	64.6	0.6	0.56	0.05	0.09	1.1	0.3	0.1	50	31	0	17	1,760
2	24.9	0.5	4.2	64.1	.9	.04	.25	.00	5.3	.3	5.3	22	55	10	1	1,960
3	22.0	2.5	5.7	67.6	1.1	.02	.11	.01	1.1	.3	0.7	63	16	11	7	2,260
4	22.3	2.5	5.8	64.0	2.8	.09	1.32	.51	0.9	.3	.4	47	29	11	8	1,850
5	22.8	4.3	5.0	62.8	2.9	.05	1.05	.37	.9	.4	.2	42	34	6	13	1,830
6	22.1	2.5	5.4	64.7	2.6	.62	0.53	.18	1.3	.2	.9	52	24	10	8	1,780
7	21.7	2.2	6.8	65.2	2.7	.18	.18	.32	0.7	.3	.8	50	25	14	7	1,840
8	22.4	4.6	5.0	64.8	2.1	.17	.20	.30	.4	.2	1.0	49	27	6	14	1,850
9	22.8	5.3	4.0	64.7	1.4	.87	.09	.35	.5	.5	0.1	55	24	2	16	1,850
10	26.0	2.8	2.6	65.8	1.5	.13	.26	.12	.8	.3	.8	45	40	2	9	1,820
11	22.4	2.3	5.9	64.4	3.7	.43	.37	.12	.7	.5	.4	47	28	12	7	1,910
12	21.6	3.9	6.7	64.7	1.3	.12	.75	.28	.8	.3	.7	46	27	11	12	1,820

[a] Potential values calculated with corrections only for free CaO.

2. ADDITION AGENTS

The cements were prepared by adding a finely ground commercial gypsum (46.7 percent of SO_3, 20.1-percent ignition loss) to the ground clinkers in such amount that the mixtures contained 1.75 percent of SO_3 as gypsum. Agreement of the analytical determinations of SO_3 made on random samples indicated that uniform mixtures were obtained when the clinker-gypsum composite had been mixed for 2 hours in a ball mill containing a few pebbles. Such mixing had no detectable effect on fineness.

The following materials in percentages by weight of clinker were dissolved in the mixing water used in preparing pastes:

Calcium chloride	[2] 1.456
Calcium acetate	[2] 1.347
Fluosilicic acid	[2] 0.330
Sugar	.050
Tannic acid	.200
Triethanolamine	.100

T D A, defined by its manufacturer as a mixture of "triethanolamine and highly purified soluble salts of modified lignin sulfonic acids," was dissolved in water (1 T D A:7H_2O by weight) and the solution sprinkled on the ground clinker. The mixture, which contained 0.033 percent of T D A and 0.23 percent of added water, was immediately placed in a ball mill with a few pebbles and mixed for 2 hours. It was not used for making up pastes until about 24 hours after mixing.

III. EXPERIMENTAL PROCEDURE

1. PREPARATION AND FILTRATION OF PASTES

A batch of 7,000 g of clinker or cement, plus 2,450 g of water (cement-water ratio=2.86) or solution containing the addition agent, was mixed by hand for 2½ minutes. Immediately after completion of the mixing, the paste was placed in a specially constructed air-pressure filter, previously described [1], and as much of the solution was removed as was permitted by the water retentivity of the paste. The average time of contact of hydrating clinker and solution was about 7 minutes. A second corresponding mixture was also prepared. This was aged for 1 hour and 55 minutes and then remixed and filtered as the first.

The quantities and colors of the filtrates were observed and recorded. In order to remove the air which had dissolved during the pressure filtration, all solutions were refiltered through a hardened filter paper into a partially evacuated flask. This procedure eliminated the formation of bubbles in the conductivity and surface-tension cells and in the picnometer. Precautions against contamination of the filtrates by the CO_2 of the air were taken by the use of soda-lime tubes.

2. CHEMICAL ANALYSES OF FILTRATES

The filtrates were aliquoted into desired amounts for the various analytical procedures shortly after filtration. The basicity was obtained by titrating the filtrates with standardized HCl, using phenolphthalein as the indicator. The average time of contact of the other

[2] Anhydrous basis.

aliquots of the basic solutions with glass receptacles prior to addition of HCl was about 20 minutes. The solutions were analyzed for the following constituents: SiO_2, R_2O_3, CaO, MgO, SO_3, Na_2O, and K_2O. The amounts of Al_2O_3 and Fe_2O_3 were generally determined when the R_2O_3 precipitate was comparatively large. Cr_2O_3 was estimated when its presence was indicated by a green color of the ignited R_2O_3. In addition to these, the amounts of Cl, CH_3COO, and F were determined when calcium chloride, calcium acetate, and fluosilicic acid, respectively, had been added to the mixing water.

Standard procedures of analysis were followed, blank determinations being made and proper corrections applied. SiO_2, R_2O_3, CaO, MgO, Na_2O, K_2O, SO_3, and Cl were determined gravimetrically. Cr_2O_3 was estimated colorimetrically. Fe_2O_3 was determined volumetrically by titration with $K_2Cr_2O_7$. Na_2O was precipitated and weighed as sodium uranyl zinc acetate. K_2O was precipitated as potassium chlorplatinate, which was reduced to Pt and the Pt weighed. Acetate was determined titrametrically on distillates from mixtures of the original solutions plus H_3PO_4 [5]. Fluorine was determined according to a method reported by Hoffman and Lundell [6].

3. pH AND OTHER CONSTANTS OF FILTRATES

Immediately after filtration, portions of the solutions were transferred to the receptacles used in the determination of pH, conductivity, surface tension, and density. These were placed in an air bath, which maintained the temperature of the solutions at 25° ± 0.03° C.

The determinations of pH were made by measuring the emf of the cell, E_c,

$$\mathrm{Pt(Pd\ black)H_2(g)|H^+(solution)}\underset{E_1}{|}\mathrm{KCl(saturated)}\underset{E_2}{|}\mathrm{Hg_2Cl_2|Hg}\ (E_0)$$

at 25° C with a calibrated potentiometer, using a sensitive galvanometer and a standard cell. Details of the apparatus, including the cell setup, have been described [7]. The pH values of the solutions, after the values of E_c had been measured, were computed from the relation,

$$\mathrm{pH}=\frac{E_c-(E_1+E_2+E_0)}{0.05914},$$

in which E_0 is the standard potential of the saturated calomel electrode, and E_1 and E_2 represent the potentials that are developed at the liquid junctions designated in the cell setup.

The values of the liquid-junction potentials, E_1 and E_2, may be approximated by the use of the modified Henderson equation [8]. However, the computations of the value of E_1 are extensive and yield only a fair approximation for complex solutions such as those obtained in this study. Instead of using a reported value for E_0 and correcting for the liquid junction potentials by Henderson's equation, an alternate method was employed as described below.

The cell was standardized against solutions of potassium hydroxide, the pH values of which were computed by Hamer [9][3] and are given in table 2. The voltages, E_c, of the cell for various concentrations of potassium hydroxide solution, ranging from 0.05 to 0.5 *N* were measured. The standard pH (designated as pH_s) for each concen-

[3] In computing the pH values, Hamer used the best reported values [10] for the activity coefficients of potassium hydroxide, and the ionization constant of water, K_w, equal to 1.008×10^{-14} at 25°C [11].

tration of potassium hydroxide was then obtained from a pH, curve of Hamer's data. Having the value of this standard pH, and the emf of the cell, E_c, for a given potassium hydroxide solution, the voltage of the calomel electrode, including the two liquid-junction potentials ($E_0+E_1+E_2$) represented by E_{cal} was computed from the relation

$$E_{cal}=E_c-0.05914\ \mathrm{pH}_s.$$

TABLE 2.—*Concentrations of solutions of potassium hydroxide and their* pH *values computed by Hamer* [9]

Concentration	pH	Concentration	pH	Concentration	pH
Moles/1,000 g of solvent		*Moles/1,000 g of solvent*		*Moles/1,000 g of solvent*	
0.05	12.61	0.35	13.41	2.00	14.25
.10	12.90	.50	13.56	3.00	14.51
.15	13.06	.75	13.74	4.00	14.73
.25	13.27	1.00	13.88		

The E_{cal} values for the range of potassium hydroxide concentrations from 0.05 to 0.5 N were found to vary systematically between 0.2346 and 0.2354 v. The extremes of this range represent a difference in pH of 0.01 units. Since the use of the average value for E_{cal} of 0.2350 v would introduce a maximum error of only 0.01 pH unit, all reported values of pH were computed from the equation

$$\mathrm{pH}=\frac{E_c-0.2350}{0.05914}.$$

During use, the cell setup was readily checked against a solution of KOH of known strength. Such calibration was found to be far more satisfactory than that obtained by the use of potassium acid phthalate buffer.

Conductivities were measured with calibrated equipment, and the results are accurate to about 0.1 percent.

The capillary-rise method was employed in the surface-tension measurements, the cell being calibrated with water, using the value of 71.98 dynes/cm [12]. The results on solutions of pure salts were reproducible to ± 0.03 dyne/cm, but the filtrates from the clinker pastes frequently contained surface contaminants, presumably traces of oil picked up during filtration, and therefore the errors for such solutions were high.

The densities of the filtrates, determined according to standard procedure and corrected to vacuum, are accurate to about 1 part in 10,000.

IV. RESULTS AND DISCUSSION

1. GENERAL EXPERIMENTAL RESULTS

The data for the filtrates are reported in table 3. All the results are for single determinations only. However, in a few scattered instances duplicate analyses of a given filtrate were made for one or more of the following: CaO, SO_3, Na_2O, K_2O, and basicity. The results of these tests agreed within 1 percent or less of the amounts reported, except those for Na_2O when present in small amounts or when present with much K_2O. These differences were generally larger, ranging up to 10 percent (clinker 4).

TABLE 3.—*Chemical composition and physical properties of the aqueous phase of Portland cement clinker pastes with and without added materials*

fy=faint yellow. fb=faint blue.
y=yellow. b=blue.
c=colorless. vfb=very faint blue.
w(c)=white (colloidal).

Added material	None		Gypsum		Calcium chloride		Calcium acetate		Fluosilicic acid		Sucrose		T D A		Tannic acid		Triethanolamine	
Filtered at	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	CLINKER 1																	
wt of soln. (g)	845	865	940	775	595	645	515	500	865	855	1055	810	1005	870	975	840	690	390
Color	fy	fy	fy	y	c	c	w(c)	c	y	y	fy	fy	y	fy	y	fy	fb	fb
Surface tension (dynes/cm)	71.65	71.66	71.75	71.86	73.02	72.85	72.13	72.00	71.92	71.98	71.42	71.85	72.10	71.66	72.03	71.69	71.77	71.91
Density (g/ml)	0.9995	1.0005	1.0014	1.0022	1.0302	1.0247	1.0195	1.0181	0.9992	1.0003	0.9999	1.0005	1.0001	1.0006	0.0996	0.0006	1.0011	1.0035
pH	12.68	12.72	12.62	12.66	12.03	12.16	12.29	12.33	12.49	12.69	12.64	12.72	12.64	12.70	12.67	12.74		
Specific conductivity (Ω^{-1})	0.01210	0.01401	0.01178	0.01424	0.06165	0.05350	0.02503	0.02473	0.0816	0.01328	0.01095	0.01391	0.01160	0.01426	0.00919	0.01403	0.01227	0.02670
SiO_2 (g/liter)	.000	.000	.002	.002	.000	.000	.004	.004	.008	.003	.002	.022	.000	.000	.000	.000	.000	.000
R_2O_3 (g/liter)	.002	.004	.003	.004	.002	.002	.005	.004	.002	.001	.003	.007	.017	.005	.012	.003	.908	.320
Al_2O_3 (g/liter)																	.566	.256
Fe_2O_3 (g/liter)																	.342	.064
CaO (g/liter)	1.73	1.47	2.22	2.30	20.59	16.48	14.01	12.39	1.16	1.39	1.58	1.42	1.63	1.55	1.31	1.42	1.41	.65
SO_3 (g/liter)	0.02	0.03	0.96	1.05	0.01	0.00	0.00	0.00	0.01	0.00	0.02	0.03	0.02	0.02	0.04	0.01	0.01	.01
Na_2O (g/liter)	.07	.59	.06	0.27	.25	.83	.21	.98	.05	.56	.05	.66	.12	.59	.07	.66	.21	2.81
K_2O (g/liter)	.92	.09	.02	.07	.05	.07	.00	.05	.01	.03	04	.09	.02	.04	.04	.08	.00	0.04
Cl (g/liter)					24.56	19.81												
CH_3COO (g/liter)							26.95	25.12										
F (g/liter)									.00	.00								
Basicity (OH^-) (equiv/liter)	.063	.069	.054	0.061	0.041	0.050	0.048	0.049	0.040	.065	.056	.068	.060	.071	.046	.070	.077	.140

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TABLE 3.—*Chemical composition and physical properties of the aqueous phase of Portland cement clinker pastes with and without added materials—Continued*

Added material	None		Gypsum		Calcium chloride		Calcium acetate		Fluosilicic acid		Sucrose		T D A		Tannic acid		Tri-ethanolamine	
Filtered at	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	CLINKER 2																	
wt of soln. (g)	660	590	980	835	945	435	835	635	615	600	845	500	855	630	235	520	430	535
Color	e	c	fy	fy	fy	fy	w (c)	c	c	c	c	c	fy	y	c	c	fb	fb
Surface tension (dynes/cm)	72.00	72.04	71.99	72.02	72.91	72.67	71.67	72.23	01.91	71.90	------	71.96	71.91	72.00	71.83	71.96	71.85	71.80
Density (gm/ml)	1.0001	1.0005	1.0017	1.0022	1.0293	1.0236	1.0191	1.0181	0.9992	1.003	1.0000	1.0005	1.0002	1.0004	0.9993	1.0005	1.0001	1.0009
pH	12.66	12.73	12.64	12.67	12.12	12.09	12.29	12.35	12.59	12.69	12.62	12.72	12.67	12.69	12.53	12.67	------	------
Specific conductivity (Ω^{-1})	0.01261	0.01477	0.01258	0.01462	0.06084	0.05213	0.02504	0.02502	0.0100	0.01360	0.01112	0.01454	0.01295	0.01425	0.00906	0.01446	0.01094	0.01483
SiO_2 (g/liter)	.000	.000	.002	.001	.004	.004	.002	.003	.003	.001	.000	.001	.000	.013	.000	.001	.000	.000
R_2O_3 (g/liter)	.001	.002	.005	.005	.003	.003	.002	.002	.002	.001	.024	.004	.002	.003	.005	.003	[a]1.215	[a].668
Al_2O_3 (g/liter)	------	------	------	------	------	------	------	------	------	------	.024	------	------	------	------	------	1.16	.66
Fe_2O_3 (g/liter)	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	0.024	.007
CaO (g/liter)	1.27	1.11	2.00	2.14	19.92	15.85	13.66	12.60	1.11	1.20	1.19	1.15	1.42	1.26	.93	1.20	.61	.52
SO_3 (g/liter)	0.00	0.00	1.13	1.16	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	.00	0.00	.01	.01
Na_2O (g/liter)	.13	.19	0.09	0.12	.10	.15	.09	.14	.06	.12	.10	.19	.11	.17	.09	.16	.11	.20
K_2O (g/liter)	.43	.95	.29	.54	.33	.72	.45	.73	.40	.89	.30	.71	.49	.88	.13	.69	.55	.95
Cl (g/liter)	------	------	------	------	23.78	19.35	------	------	------	------	------	------	------	------	------	------	------	------
CH_3COO (g/liter)	------	------	------	------	------	------	27.11	25.12	------	------	------	------	------	------	------	------	------	------
F (g/liter)	------	------	------	------	------	------	------	------	.001	.001	------	------	------	------	------	------	------	------
Basicity (OH^-) (equiv/liter)	.062	.069	.056	.066	0.048	0.043	0.048	0.051	.049	.065	.055	.069	.065	.069	.043	.069	.066	.083

[a] V_2O_3 present in small amounts.

CLINKER 3

CLINKER 3

wt of soln (g)	710 e	725 e	820 fy	625 fy	640 fy	440 e	505 (w) e	285 e	505 e	675 e	615 e	685 e	665 e	685 e	525 e	600 e	265 b	465 b
Color																		
Surface tension (dynes/cm)	72.040	72.00	71.93	72.00	72.75	72.56			71.83	71.92	72.00	71.98						
Density (g/ml)	1.002	1.0002	1.0019	1.0016	1.0265	1.0196	1.0135	1.0108	0.9999	1.0002	1.0003	1.0003	1.0001	1.0007	1.0001	1.0000	1.0008	1.0011
pH	12.67	12.67	12.63	12.61	12.17	12.15	12.41	12.27	12.62	12.60	12.68	12.68			12.67	12.66		
Specific conductivity (Ω^{-1})	0.01252	0.01251	0.01323	0.01272	0.05650	0.04495	0.02209	0.01873	0.01098	0.01166	0.01304	0.01298	0.01285	0.01302	0.01269	0.01262	0.01004	0.01501
SiO_2 (g/liter)	.001	.000	.001	.000	.000	.004	.002	.002	.001	.000							.002	.001
R_2O_3 (g/liter)	.004	.005	.004	.006	.005		.001	.003	.003	.001							.273	.137
Al_2O_3 (g/liter)																	.154	.113
Fe_2O_3 (g/liter)																	.119	.024
CaO (g/liter)	1.58	1.52	2.34	2.17	18.40	13.68	10.01	8.07	1.44	1.43	1.58	1.48	1.64	1.57	1.60	1.50	1.16	1.51
SO_3 (g/liter)	0.00	0.00	1.02	1.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O (g/liter)	.06	.07	0.05	0.05	.05	.11	.08	.14	.02	.05	.10	.14	.07	.11	.08	.09	.10	.18
K_2O (g/liter)	.28	.31	.17	.26	.19	.39	.32	.49	.16	.30	.36	.45	.33	.40	.31	.37	.39	.68
Cl (g/liter)					21.17	15.93												
CH_3COO (g/liter)							18.13	15.38										
F (g/liter)									.00	.00								
Basicity (OH^-) (equiv/liter)	.064	.063	.063	.059	0.056	0.045	0.055	0.038	.056	.058	.066	.065	.066	.065	.065	.063	.068	.086

CLINKER 4

wt of soln (g)	660 y	600 y	670 y	665 y	580 c	620 c	515 c	475 c	535 y	535 y	405 c	450 c	735 y	695 y	285 y	365 fy		265 b
Color																		
Surface tension (dynes/cm)	72.26	72.28	72.27	72.25	72.88	72.85	72.51	72.33	72.18	72.66	72.25	72.75	72.33	72.34	72.21	72.30		72.58
Density (g/ml)	1.0216	1.0206	1.0239	1.0254	1.0295	1.0272	1.0224	1.0235	2.0187	1.0192	1.0218	1.0232	1.0235	1.0216	1.0198	1.0213		1.0256
pH	13.19	13.41	12.99	13.07	12.32	12.44	12.91	12.93	13.13	13.46		13.58	13.00	13.30	13.26	13.49		
Specific conductivity (Ω^{-1})	0.06565	0.08800	0.05445	0.06040	0.07520	0.07380	0.05310	0.05545	0.05810	0.09360	0.1102	0.1172	0.05484	0.07420	0.06790	0.1092		0.1232
SiO_2 (g/liter)	.025	.012	.008	.008	.008	.007	.00	.00	.007	.001	.016	.065	.005	.011	.047	.031		.059
R_2O_3 (g/liter)	.033	.018	.060	.061	.006	.001	.002	.007	.045	.007	.231	.019	.043	.041	.057	.011		.286
Al_2O_3 (g/liter)											.231	.019						.051
Fe_2O_3 (g/liter)																		.235
Cr_2O_3 (g/liter)	.030	.015	.050	.050					.025	.005			.035	.035	.025			
CaO (g/liter)	.23	.21	1.00	1.05	7.13	4.61	1.69	1.26	.12	.05	.05	.10	.66	.35	.10	.11		.07
SO_3 (g/liter)	7.90	3.35	11.72	11.74	0.04	0.01	0.04	0.05	6.89	.56	.10	.10	11.40	6.57	6.14	.16		.06
Na_2O (g/liter)	0.48	0.79	0.35	0.52	.42	.45	.33	.48	0.12	.21	.75	.92	0.20	0.26	0.28	.28		2.47
K_2O (g/liter)	18.65	19.71	18.23	19.34	21.08	22.74	21.74	23.46	17.02	20.09	22.22	23.35	18.18	19.63	18.30	22.25		25.77
Cl (g/liter)					23.61	21.65												
CH_3COO (g/liter)							25.46	26.38										
F (g/liter)									0.11	0.18								
Basicity (OH^-) (equiv/liter)	0.213	0.358	0.134	0.162	0.048	0.052	0.103	0.102	.184	.397	0.492	0.524	0.135	0.276	0.240	0.485		0.570

TABLE 3.—*Chemical composition and physical properties of the aqueous phase of Portland cement clinker pastes with and without added materials—Continued*

Added material	None		Gypsum		Calcium chloride		Calcium acetate		Fluosilicic acid		Sucrose		T D A		Tannic acid		Tri-ethanolamine	
Filtered at	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	CLINKER 5																	
wt of soln (g)	495	605	620	660	625	575	425	630	405	465	245	520	635	735	285	465	.....	325
Color	y	c	y	y	c	c	c	c	y	c	c	c	y	y	y	c	.....	b
Surface tension (dynes/cm)	72.20	72.02	72.08	72.24	72.95	72.75	72.28	.....	71.92	72.11	72.09	72.50	72.12	72.29	71.96	72.39	.....	72.05
Density (g/ml)	1.0126	1.0133	1.0159	1.0171	1.0297	1.0277	1.0193	1.0205	1.0112	1.0134	1.0128	1.0154	1.0154	1.0150	1.0126	1.0145	.....	1.0167
pH	13.19	13.39	12.91	13.04	12.24	12.29	12.54	12.68	12.97	13.38	13.31	13.43	12.91	13.13	13.08	13.39	.....	.....
Specific conductivity (Ω^{-1})	0.05520	0.07555	0.04160	0.04870	0.07070	0.06875	0.03928	0.04152	0.04085	0.07390	0.07045	0.08415	0.04120	0.05275	0.04700	0.07950	.....	0.08395
SiO_2 (g/liter)	.029	.015	.005	.004	.003	.002	.007	.000	.006	.000	.028	.020	.007	.022	.028	.030	.....	.048
R_2O_3 (g/liter)	.023	.005	.031	.029	.007	.006	.007	.003	.030	.026	.283	.013	.042	.027	.054	.012	.....	.500
Al_2O_3 (g/liter)	.....	.....	.....	.....	.....	.....	.....	.....	.....	.026	.283	.013	.....	.....	.....	.....	.....	.045
Fe_2O_3 (g/liter)	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.455
Cr_2O_3 (g/liter)	.010	.....	.030	.025	.....	.....	.....	.....	.015	.....	.....	.....	.....	.....	.030	.....	.....	.....
CaO (g/liter)	.12	.15	.96	1.09	11.48	9.49	4.69	4.46	.17	.06	.04	.13	.65	.42	.13	.10	.....	.06
SO_3 (g/liter)	2.81	.13	7.76	7.45	0.04	0.02	0.02	0.01	3.99	.11	.15	.08	7.53	5.15	4.08	.09	.....	.09
Na_2O (g/liter)	0.11	.17	0.09	0.13	.12	.16	.18	.23	0.06	.20	.22	.34	0.10	0.14	0.12	.42	.....	.47
K_2O (g/liter)	13.21	15.08	12.90	13.92	14.15	15.89	14.71	16.20	11.49	15.49	14.38	16.91	13.09	14.13	12.84	16.14	.....	17.72
Cl (g/liter)	.....	.....	.....	.....	23.85	22.31	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
CH_3COO (g/liter)	.....	.....	.....	.....	.....	.....	24.49	25.91	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
F (g/liter)	.....	.....	.....	.....	.....	.....	.....	.....	0.09	0.16	.....	.....	.....	.....	.....	.....	.....	.....
Basicity (OH^-) (equiv/liter)	0.211	0.328	0.110	0.148	0.048	0.046	0.061	0.066	.132	.315	0.307	0.366	0.109	0.181	0.163	0.347	.....	0.381

CLINKER 6

CLINKER 6

wt of soln (g)	480	535	670	635	670	555	660	550	560	525	435	545	755	735	295	520		440
Color	fy	c	y	y	c	c	w (c)	c	c	c	c	c	y	y	fy	c		b
Surface tension (dynes/cm)	71.80	72.21	72.08	72.33	72.95		72.34	72.31	72.14	72.26	72.20	72.23	72.29	72.23	72.23	72.34		72.38
Density (g/ml)	1.0007	1.0098	1.0094	1.0120	1.0271	1.0273	1.017	1.0183	1.0064	1.0095	1.0095	1.0122	1.0090	1.0097	1.0069	1.0108		1.0155
pH	13.12	13.29	12.92	12.97	12.21	12.33	12.61	12.63	13.14	13.29	13.17	13.36	13.03	13.21	13.18	13.32		
Specific conductivity (Ω^{-1})	0.04195	0.05890	0.03318	0.03818	0.06280	0.05890	0.03298	0.03505	0.04260	0.05785	0.05670	0.07020	0.03830	0.05085	0.04540	0.06380		0.08090
SiO_2 (g/liter)	.011	.014	.005	.022	.002	.014	.002	.000	.005	.000	.006	.005	.007	.005	.003	.005		.014
R_2O_3 (g/liter)	.005	.007	.017	.018	.004	.006	.014	.004	.014	.004	.325	.007	.021	.010	.055	.043		.331
Al_2O_3 (g/liter)											.325	.007						.043
Fe_2O_3 (g/liter)																		.288
Cr_2O_3 (g/liter)	.005		.010	.010									.010	.005				
CaO (g/liter)	.17	.23	1.17	1.10	12.42	8.80	5.76	5.16	.11	.12	.07	.17	.45	.41	.11	.20		.12
SO_3 (g/liter)	.80	.06	4.13	5.34	0.01	0.01	0.02	0.01	.26	.05	.03	.03	2.97	1.32	0.15	.02		.02
Na_2O (g/liter)	2.20	3.37	2.05	2.87	2.93	3.92	3.37	3.97	2.27	3.51	3.43	4.53	2.43	3.00	2.41	3.83		5.74
K_2O (g/liter)	5.99	7.22	5.25	6.23	6.46	7.41	6.66	7.27	5.37	6.67	6.73	7.68	5.88	6.50	5.56	7.25		8.88
Cl (g/liter)					22.03	19.46												
CH_3COO (g/liter)							23.15	24.26										
F (g/liter)									0.06	0.08								
Basicity (OH^-) (equiv/liter)	0.179	0.266	0.116	0.131	0.048	0.050	0.062	0.063	.184	.258	0.259	0.322	0.146	0.219	0.200	0.290		0.390

CLINKER 7

wt of soln (g)	330	350	525	470	610	325	365	115	235	355	330	375	365	395	345	385		
Color	c	c	fy	fy	c	c	w (c)	c	c	c	c	c	c	c	c	c		
Surface tension (dynes/cm)	72.00	72.04	72.00	72.00	72.88	72.46	72.25		71.9	72.00	72.01	71.97	71.97	72.04	71.98	72.01		
Density (g/ml)	1.0027	1.0035	1.0044	1.0046	1.0250	1.0176	1.0113	1.0052	1.0017	1.0035	1.0032	1.0042	1.0023	1.0034	1.0027	1.0038		
pH	13.10	13.16	12.85	12.79	12.17	12.19	12.47	12.65	12.88	13.00	12.99	13.05	12.91	13.00	12.95	13.03		
Specific conductivity (Ω^{-1})	0.02660	0.03050	0.02139	0.02156	0.05610	0.04400	0.02314	0.02092	0.02245	0.03080	0.02872	0.03377	0.02433	0.02981	0.02666	0.03192		
SiO_2 (g/liter)	.001	.002	.001	.001	.000	.000	.005	.007	.001	.002	.003	.001	.002	.005	.004	.005		
R_2O_3 (g/liter)	.003	.003	.006	.002	.006	.001	.007	.027	.016	.005	.017	.003	.014	.009	.018	.005		
CaO (g/liter)	.40	.33	1.57	1.44	15.17	9.80	6.02	.75	.20	.27	.27	.32	.57	.47	.32	.36		
SO_3 (g/liter)	.02	.00	1.91	2.03	0.00	0.00	0.02		.02	.01	.00	.00	.01	.01	.00	.00		
Na_2O (g/liter)	1.26	1.57	0.87	0.97	.98	1.38	1.29	2.15	1.13	1.74	1.58	1.96	1.05	1.54	1.41	1.79		
K_2O (g/liter)	2.84	3.20	2.26	2.66	2.59	3.14	2.82	3.82	2.46	3.34	3.17	3.84	2.63	3.25	2.99	3.22		
Cl (g/liter)					20.30	14.69												
CH_3COO (g/liter)							15.39	7.07										
F (g/liter)									0.02	0.02								
Basicity (OH^-) (equiv/liter)	0.117	0.136	0.085	0.084	0.052	0.042	0.052	0.056	.097	.135	0.126	0.150	0.109	0.133	0.118	0.143		

TABLE 3.—*Chemical composition and physical properties of the aqueous phase of Portland cement clinker pastes with and without added materials—Continued*

Added material	None		Gypsum		Calcium chloride		Calcium acetate		Fluosilicic acid		Sucrose		T D A		Tannic acid		Tri-ethanolamine	
Filtered at	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	CLINKER 8																	
wt of soln (g)	510	560	640	620	670	500	405	385	385	595	445	540	715	590	325	485	.....	215
Color	c	c	y	y	c	c	w (c)	c	c	c	c	c	fy	fy	c	c	.....	c
Surface tension (dynes/cm)	72.00	72.01	72.17	72.11	72.99	72.80	72.30	72.19	71.95	72.13	71.98	72.19	72.05	72.10	71.97	72.08	.....	71.9
Density (g/ml)	1.0035	1.0040	1.0052	1.0057	1.0259	1.0234	1.0151	1.0150	1.0022	1.0041	1.0030	1.0046	1.0042	1.0037	1.0032	1.0041	.....	1.0066
pH	13.01	13.05	12.82	12.81	12.16	12.19	12.46	12.43	12.91	13.04	12.98	13.09	.....	13.02	12.97	13.02	.....	.....
Specific conductivity (Ω^{-1})	0.03061	0.03306	0.02394	0.02504	0.05815	0.05445	0.02655	0.02655	0.02441	0.03320	0.02843	0.03591	0.02162	0.03146	0.02930	0.03302	.....	0.04322
SiO_2 (g/liter)	.002	.002	.002	.003	.000	.000	.003	.001	.001	.001	.002	.002	.001	.004	.003	.003	.....	.002
R_2O_3 (g/liter)	.006	.006	.003	.004	.010	.008	.027	.005	.009	.003	.033	.008	.015	.009	.016	.002	.....	.015
Al_2O_3 (g/liter)											.033							
CaO (g/liter)	.44	.39	1.47	1.40	14.86	12.87	7.67	7.38	.23	.36	.36	.36	.96	.48	.23	.38	.....	.25
SO_3 (g/liter)	.01	.01	2.21	2.48	0.00	0.01	0.04	0.01	0.01	.01	.00	.00	1.83	.02	.01	.00	.....	.01
Na_2O (g/liter)	1.46	1.65	1.08	1.25	1.39	1.62	1.51	1.74	1.13	1.71	1.38	1.93	1.01	1.49	1.52	1.69	.....	2.55
K_2O (g/liter)	3.35	3.48	3.07	3.34	3.33	3.87	3.67	3.92	3.01	3.46	3.11	3.76	3.11	3.62	3.49	3.83	.....	4.96
Cl (g/liter)	.....	.....	.....	.....	21.27	19.23	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
CH_3COO (g/liter)	.....	.....	.....	.....	.....	.....	20.20	20.86	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
F (g/liter)	.....	.....	.....	.....	.....	.....	.....	.....	0.02	0.03	.....	.....	.....	.....	.....	.....	.....	.....
Basicity (OH^-) (equiv/liter)	0.136	0.147	0.093	0.095	0.047	0.048	0.054	0.049	.105	.147	0.125	0.161	0.081	0.140	0.129	0.147	.....	0.205

CLINKER 9

CLINKER 9

wt of soln (g)	475	665	585	630	650	480	340	525	565	565	535	620	840	710	705	540	125	230
Color	c	c	y	y	c	c	c	c	fy	c	fy	c	y	fy	y	c	c	b
Surface tension (dynes/cm)	72.13	72.24	72.18	72.16	72.96	72.83	72.43	72.38		72.26	72.13	72.31	72.00	72.27	72.10	72.20	71.95	72.44
Density (g/ml)	1.0030	1.0037	1.0045	1.0056	1.0248	1.0228	1.0156	1.0150	1.0012	1.0037	1.0021	1.0038	1.0036	1.0032	1.0023	1.0037	1.0032	1.0105
pH	12.98	13.03	12.78	12.80	12.20	12.20	12.65	12.66	12.73	13.01	12.91	13.04	12.78	12.92	12.82	13.03		
Specific conductivity (Ω^{-1})	0.02762	0.03158	0.02148	0.02390	0.05595	0.05280	0.02600	0.02630	0.01759	0.03060	0.02330	0.03178	0.02060	0.02693	0.02053	0.03139	0.02497	0.06040
SiO_2 (g/liter)	.000	.001	.001	.002	.001	.002	.002	.000	.001	.002	.003	.003	.002	.002	.003	.004	.002	.005
R_2O_3 (g/liter)	.003	.001	.008	.009	.006	.008	.033	.011	.007	.004	.011	.004	.016	.009	.007	.002	.593	.088
Cr_2O_3 (g/liter)			.005	.005											.005			
CaO (g/liter)	.80	.43	1.44	1.31	14.21	12.15	8.27	7.07	.50	.52	.58	.45	1.24	.85	.69	.39	.28	.14
SO_3 (g/liter)	.00	.00	2.08	2.55	0.01	0.01	0.03	0.00	.31	.01	.08	.01	1.55	.16	.68	.01	.01	.01
Na_2O (g/liter)	2.99	3.89	2.53	3.27	3.94	4.77	3.85	4.82	2.11	3.84	2.71	3.96	2.55	3.06	2.50	4.00	3.45	8.83
K_2O (g/liter)	0.35	0.35	0.28	0.33	0.33	0.34	0.30	0.29	0.21	0.44	0.34	0.31	0.26	0.31	0.25	0.31	0.38	0.60
Cl (g/liter)					20.70	19.25												
CH_3COO (g/liter)							21.40	21.11										
F (g/liter)									.03	.03								
Basicity (OH−) (equiv/liter)	.133	.150	.089	.096	0.050	0.047	0.059	0.056	.079	.145	.109	.151	.088	.128	.092	.147	.13	.31

CLINKER 10

wt of soln (g)	605	695	700	665	795	555	495	460	515	640	525	605	905	730	450	635	350	485
Color	c	c	fy	vfy	c	c	w (c)	w (c)	c	c	c	c	fy	c	c	c	vfb	fb
Surface tension (dynes/cm)	71.99	72.21	72.11	72.21	73.16	73.00			71.96	72.03	72.25	72.16	72.16	72.17	71.96	72.10	71.96	71.97
Density (g/ml)	1.0011	1.0011	1.0028	1.0028	1.0280	1.0260	1.0185	1.0170	1.0008	1.0008	1.0014	1.0012	1.0012	1.0011	1.0011	1.0010	1.0018	1.0023
pH	12.81	12.80	12.72	12.71	12.15	12.14	12.61		12.85	12.86	12.82	12.79	12.71	12.76	12.80	12.80		
Specific conductivity (Ω^{-1})	0.01783	8.01773	0.01705	0.01678	0.06000	0.05675	0.02539	0.02467	0.01598	0.01656	0.01882	0.01824	0.01557	0.01717	0.01771	0.01758	0.01778	0.02178
SiO (g/liter)	.001	.003	.003	.003	.002	.003	.151	.070	.001	.002	.002	.002	.002	.002	.002	.001	.005	.003
R_2O_3 (g/liter)	.005	.013	.005	.004	.011	.011	.494	.232	.003	.002	.003	.002	.004	.003	.003	.000	.274	.083
Al_2O_3 (g/liter)							.417	.216									.014	.003
Fe_2O_3 (g/liter)							.077	.016									.260	.080
CaO (g/liter)	1.28	1.03	2.03	1.87	18.28	16.69	12.43	11.06	1.35	1.00	1.50	1.03	1.41	1.21	1.33	1.03	1.38	1.04
SO_3 (g/liter)	0.01	0.02	1.29	1.37	0.00	0.00	0.24	0.13	0.00	0.00	0.01	0.01	0.38	0.01	0.01	0.01	0.00	0.00
Na_2O (g/liter)	.24	.34	0.18	0.23	.30	.40	.34	.39	.15	.26	.22	.35	.15	.22	.23	.32	.27	.58
K_2O (g/liter)	1.45	1.83	1.40	1.63	1.61	1.84	1.70	1.90	1.26	1.65	1.59	1.84	1.50	1.61	1.52	1.74	1.66	2.38
Cl (g/liter)					22.81	21.27												
CH_3COO (g/liter)							21.70	21.34										
F (g/liter)									0.00	0.01								
Basicity (OH−) (equiv/liter)	0.085	0.082	0.076	0.072	0.054	0.050	0.090	0.060	.077	.076	0.091	0.085	0.073	0.082	0.085	0.082	0.096	0.112

TABLE 3.—*Chemical composition and physical properties of the aqueous phase of Portland cement clinker pastes with and without added materials—Continued*

Added material	None		Gypsum		Calcium chloride		Calcium acetate		Fluosilicic acid		Sucrose		TDA		Tannic acid		Triethanolamine	
Filtered at	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	min	2 hr	7 min	2 hr
	CLINKER 11																	
wt. of soln. (g)	405	345	585	550	575	310	325	400	270	435	340	365	540	535	390	330	220	145
Color	e	e	fy	fy	e	e	w (e)	e	e	e	e	e	e	vfy	e	e	b	b
Surface tension (dynes/cm)	72.18	72.15	72.13	72.18	73.00	72.85	72.41	72.43	72.15	72.31	72.33	72.48	72.21	72.20	72.28	71.91	71.91	71.75
Density (g/ml)	1.0037	1.0042	1.0045	1.0045	1.0259	1.0197	1.0139	1.0123	1.0025	1.0043	1.0044	1.0052	1.0024	1.0038	1.0034	1.0043	1.0063	1.0068
pH	13.02	13.03	12.80	12.79	12.20	12.17	12.50	12.48	12.91	13.04	13.06	13.06	12.89	12.99	12.96	13.02	------	------
Specific conductivity (Ω^{-1})	0.03131	0.03358	0.02202	0.02189	0.05760	0.04762	0.02562	0.02458	0.02559	0.03469	0.03466	0.03829	0.02436	0.03121	0.02997	0.03372	0.03911	0.04166
SiO_2 (g/liter)	.006	.001	.003	.003	.005	.004	.001	.000	.007	.003	.002	.003	.003	.002	.013	.004	.025	.020
R_2O_3 (g/liter)	.004	.001	.006	.007	.003	.005	.009	.006	.023	.004	.025	.007	.007	.009	.015	.004	.340	.248
Al_2O_3 (g/liter)	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	.055	.022
Fe_2O_3 (g/liter)	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	.285	.226
CaO (g/liter)	.40	.39	1.75	1.47	15.51	10.66	7.39	6.68	.19	.30	.26	.35	.77	.54	.48	.31	.10	.09
SO_3 (g/liter)	.02	.01	1.82	2.13	0.01	0.02	0.01	0.01	.01	.00	.00	.00	.03	.00	.01	.01	.01	.01
Na_2O (g/liter)	1.78	1.97	0.77	0.99	1.11	1.80	1.48	1.91	1.49	2.20	2.15	2.41	.95	1.69	1.77	2.00	2.81	3.13
K_2O (g/liter)	3.28	3.48	2.44	2.65	2.78	3.40	3.13	3.53	2.82	3.61	3.63	3.91	2.62	3.24	3.23	3.47	3.97	4.27
Cl (g/liter)	------	------	------	------	21.03	16.40	------	------	------	------	------	------	------	------	------	------	------	------
CH_3COO (g/liter)	------	------	------	------	------	------	18.06	19.07	------	------	------	------	------	------	------	------	------	------
F (g/liter)	------	------	------	------	------	------	------	------	0.00	0.02	------	------	------	------	------	------	------	------
Basicity (OH^-) (equiv/liter)	0.139	0.150	0.091	0.085	0.053	0.040	0.057	0.050	0.110	.155	0.152	0.172	0.110	0.140	0.131	0.151	0.184	0.199

wt of soln.....(g)	315	405	515	515	580	280	425	370	305	435	285	285	555	445	395	290		
Color	c	c	y	y	c	c	w (c)	c	c	c	c	c	y	fy	c	fy		
Surface tension (dynes/cm)	72.24	72.06	72.18	71.98	73.10	72.91	72.20	72.31	72.24	72.38	72.25	72.41	72.26	72.24	72.24	72.41		
Density.....(g/ml)	1.0094	1.0105	1.0112	1.0119	1.0243	1.0211	1.0143	1.0150	1.0085	1.0106	1.0105	1.0112	1.0085	1.0081	1.0095	1.0108		
pH	13.26	13.30	12.96	-------	12.30	12.29	12.71	12.68	13.19	13.29	13.36	13.33	-------	-------	13.27	13.30		
Specific conductivity (Ω^{-1})	0.05730	0.06240	0.03731	0.03748	0.06005	0.04580	0.03382	0.03513	0.05250	0.06285	0.06200	0.06590	0.03972	0.05260	0.06040	0.06340		
SiO_2.....(g/liter)	.013	.011	.001	.002	.002	.000	.000	.002	.012	.011	.011	.010	.010	.010	.005	.013		
R_2O_3.....(g/liter)	.017	.006	.020	.018	.007	.006	.004	.002	.033	.006	.023	.012	.016	.008	.025	.018		
Cr_2O_3.....(g/liter)	-------	-------	.015	.015	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------		
CaO.....(g/liter)	.15	.17	1.21	1.10	10.64	7.37	3.44	2.91	.07	.14	.12	.13	.43	.24	.13	.12		
SO_3.....(g/liter)	.02	.03	4.68	5.11	0.01	0.01	0.01	0.01	.03	.01	.02	.02	2.30	.13	.01	.01		
Na_2O.....(g/liter)	.45	.51	0.26	0.33	.28	.43	.46	.65	.28	.48	.51	.59	0.14	.26	.53	.57		
K_2O.....(g/liter)	10.73	11.66	8.95	9.32	10.26	11.81	10.98	12.22	9.73	11.81	11.62	12.16	8.82	9.69	11.06	11.89		
Cl.....(g/liter)	-------	-------	-------	-------	19.56	17.06	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------		
CH_3COO.....(g/liter)	-------	-------	-------	-------	-------	-------	17.88	19.09	-------	-------	-------	-------	-------	-------	-------	-------		
F.....(g/liter)	-------	-------	-------	-------	-------	-------	-------	-------	0.03	0.02	-------	-------	-------	-------	-------	-------		
Basicity (OH^-) (equiv/liter)	0.246	0.270	0.123	0.119	0.051	0.042	0.068	0.062	.222	.270	0.267	0.283	0.149	0.220	0.255	0.273		

Only a few random analyses were made on filtrates from duplicate pastes. These may be taken as indicative of the reproducibility of the data. The analyses of extracts from duplicate pastes obtained at 7 minutes (clinker 11 plus calcium acetate) were as follows:

	g/liter		g/liter
SiO_2	0.001	Na_2O	1.48
Do	.001	Do	1.52
R_2O_3	.009	K_2O	3.13
Do	.004	Do	3.19
CaO	7.39		
Do	7.14		
SO_3	0.01		equiv./liter
Do	.01	Basicity	0.057
		Do	.054

In general, these data show good agreement. The observed differences are due probably more to the variations of about 1 or 2 minutes in the times of contact of solution and clinker than to analytical errors. A few determinations of CaO and basicity in filtrates from duplicate pastes at 2 hours showed better agreement than those observed at 7 minutes.

The differences between the weights of the water used in making up the pastes and the weights of the filtrates given in table 3 furnish no indication of the extent of hydration of the clinkers, since most of the uncombined water could not be removed by the method used. This was particularly true of some of the 7-minute pastes, where shrinkage caused by quick setting interfered with the filtration process.

The filtrates were clear and colorless with the following exceptions: (1) A yellow color, observed in some of the extracts, was found to be associated with the presence of Cr_2O_3. (2) Triethanolamine, after reaction with the clinkers, usually imparted a light-blue color. (3) The use of calcium acetate with a number of clinkers resulted in the formation of a white colloidal solution.

MgO was generally absent from the solution (0.000 g/liter in 173 out of 204 determinations) or present only in small amounts (0.001 to 0.029 g/liter). Since no correlations involving MgO could be deduced, it will not be considered further.

Sulfite was present in solutions obtained from the pastes of clinkers 7 and 8 (no added materials). Small amounts of thiosulfate were present in the filtrates from corresponding pastes containing gypsum. No quantitative estimation of these two constituents was attempted.

2. COMPOSITIONS OF THE FILTRATES

Figure 1, plotted from data in table 3, shows the compositions of the 7-minute and 2-hour extracts from the clinker pastes containing no added materials. In this figure the basicities of the extracts and concentrations of each oxide are plotted against the potash content of the clinkers from which the extracts were obtained.

Although this method of plotting the data is somewhat empirical, it appears to be justified in that it reveals certain trends in the data. Thus the increase in concentration of potash in solution with increased potash content of the clinkers is accompanied by increased basicity; increased concentrations of silica and oxides of the R_2O_3 group; increased concentration of sulfate in the extracts from the clinkers highest in potash; and a rather irregular decrease in the lime con-

centration. The graph of soda concentrations serves only for comparison of the individual values with the concentrations of other oxides, since the quantities of extracted soda have no relation to the potash content of the clinkers.

The percentage extractions of soda from the clinkers are considerably smaller than the extractions of potash and show less relation to the soda content of the clinkers. Hence the adopted method of plotting gives more regular relations than those which result when the concentrations of the various oxides in the extracts are plotted against the total alkali content of the clinkers.

In this section the discussion will be confined to the salient trends in the concentrations of the individual oxides in the extracts from the pastes both with and without added materials. The general effects of each added material on the concentrations of all of the oxides taken as a group will be discussed in section 4, page 240.

(a) ALKALIES (K_2O AND Na_2O)

As shown by figure 1, the maximum concentrations of alkalies in the extracts from the untreated clinker pastes were 2.99 g/liter of Na_2O and 18.65 g/liter of K_2O at 7 minutes and 3.89 g/liter of Na_2O and 19.71 g/liter of K_2O at 2 hours. The relatively large amounts of K_2O in the extracts from clinkers 4, 5, 6, 11, and 12 are attributed to the presence of K_2SO_4.[4] In general, smaller amounts of alkalies were extracted in the interval between 7 minutes and 2 hours than during the first 7 minutes.

The results indicate that large differences may exist among clinkers with respect to the rate of solution of the alkalies. In all the 12 clinkers considerable amounts of alkalies remained undissolved at 2 hours. The extent of solution is best shown by calculations of the fractions (percentages of the total in the clinkers) of potash and soda that had dissolved at 7 minutes and at 2 hours.

Such calculations were made for the filtrates from the untreated pastes and from those containing gypsum and triethanolamine. These two added materials represent the extreme effects of the addition agents on the extractions of alkalies—gypsum causing the greatest decreases and triethanolamine the greatest increases. The results given in table 4 shows that the percentages of soda and potash in solution at 7 minutes varied from 0.4 to 30 and 1 to 58, respectively. Calculations based on the data in table 4 reveal that the rate of solution of K_2O from clinkers between 7 minutes and 2 hours varied between 0 and 9 percent, and of Na_2O, between 1 and 12. The values with added gypsum were slightly decreased, from 1 to 8 percent for the K_2O and 1 to 7 percent for the Na_2O. In the presence of triethanolamine, the rate of solution of the K_2O (from six clinkers) varied between 2 and 10 percent, and of Na_2O, from 2 to 21 percent.

[4] The assumption that all, or nearly all, the SO_3 is present as K_2SO_4 in clinkers 4, 5, 6, 11, and 12 is based on the following deductions, as previously reported in detail [1]. The large fractions (about 50 percent) of total K_2O dissolving in 7 minutes, together with a nearly linear relation between the SO_3 and K_2O contents of the clinkers, suggested the presence of the readily soluble salt, K_2SO_4. Supporting evidence indicating the presence of the salt in the clinkers was shown by the good agreement between the number of moles of K_2O in the extracts and the number of moles of SO_3 in the clinkers.

Reports by Taylor on phase-equilibria studies involving K_2O and SO_3 as constituents [13] and on direct examinations of commercial clinkers [14] show that K_2SO_4 generally may be observed microscopically in clinker samples if the calculated potential K_2SO_4 is more than 0.25 percent.

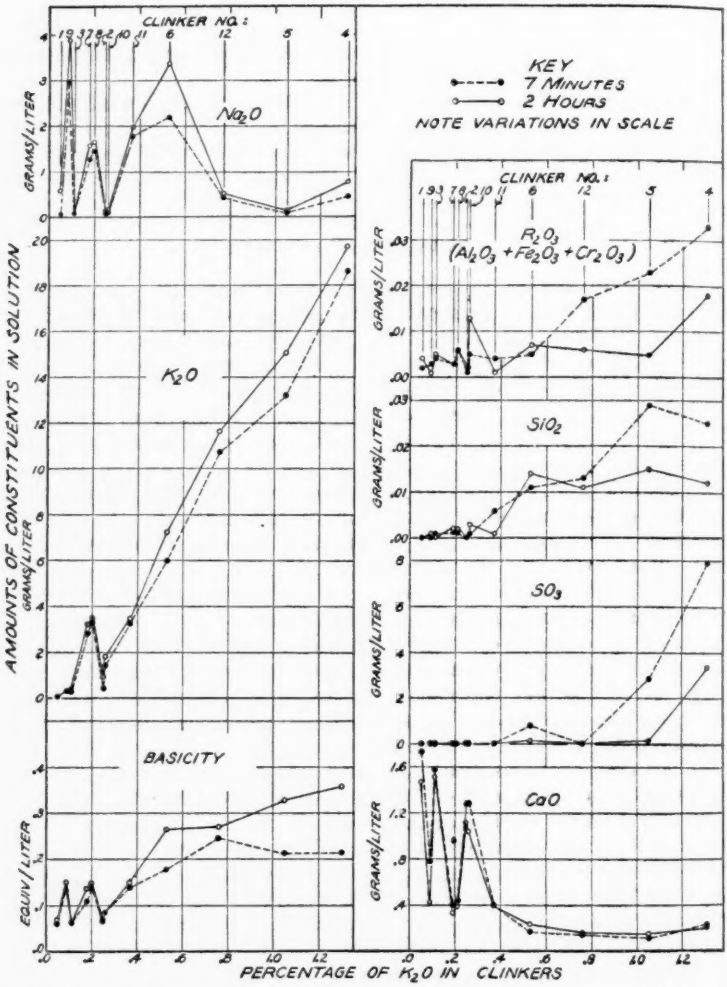

FIGURE 1.—*Amounts of constituents found in filtrates from untreated clinker pastes at 7 minutes and 2 hours*

Note variations in scale.

TABLE 4.—*Percentages of total* K_2O *and total* Na_2O *in clinkers which were found in filtrates at 7 minutes and 2 hours from pastes containing gypsum, triethanolamine, and no added materials*

Clinker	K_2O							Na_2O						
	Total in clinker	No Added material		Gypsum		Triethanolamine		Total in clinker	No Added material		Gypsum		Triethanolamine	
		7 min	2 hr	7 min	2 hr	7 min	2 hr		7 min	2 hr	7 min	2 hr	7 min	2 hr
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	0.05	1	6	1	5	1	3	0.56	0.4	3.8	0.4	1.7	1.3	18
2	.25	6	14	4	7	8	14	.04	12	18	8	11	10	18
3	.11	9	10	5	8	13	22	.02	10	12	8	9	16	31
4	1.32	50	52	48	51	------	68	.09	19	31	13	20	------	96
5	1.05	44	50	43	46	------	59	.05	8	12	7	11	------	33
6	0.53	40	49	35	41	------	59	.62	12	19	12	16	------	32
7	.18	56	62	43	51	------	------	.18	25	31	17	19	------	------
8	.20	58	61	54	59	------	87	.17	30	34	22	26	------	52
9	.09	14	14	11	13	15	23	.87	12	16	10	13	14	35
10	.26	20	25	19	22	22	32	.13	7	9	5	6	7	16
11	.37	31	33	23	25	37	40	.43	15	16	6	8	23	25
12	.70	49	54	41	42	------	------	.12	13	15	8	10	------	------

The results in table 4 were computed on the assumption that the ratio of clinker to solution remained unchanged up to 2 hours. Actually, a portion of the water had combined with the clinker during this period, having the effect of increasing the concentrations of the solutes. The extent of this hydration at time periods comparable to those used in this investigation has been studied by Forsen [15]. He reported that 5 and 6 percent of the mixing water combined as firmly fixed water (retained at 105° C) in 10 minutes and 1 hour, respectively, in the case of a quick-setting clinker gaged with 40 percent of water. Addition of a retarder (gypsum plus plaster of paris) reduced these values to 4 and 5 percent, respectively. These results are mentioned here only to indicate roughly the fraction of "fixed" water and not as correction factors. It is apparent that the amount of water removed as hydrate water will vary from clinker to clinker and with the added materials. Since no corrections were made for hydrate water, the computations are intended only as approximations of the true values.

(b) LIME

The relation of lime concentration to basicity indicated by the comparisons in figure 1 is more clearly shown in figure 2, where the amounts of lime are plotted against the values of basicity ($NaOH+KOH+Ca(OH)_2$) of the extracts from untreated pastes. The equilibrium solubility curves of lime in sodium and potassium hydroxide solutions, determined by Forsen [15], are reproduced in this figure.

The trend of the data of this study roughly parallels Forsen's solubility curves. The amounts of CaO in solution, however, exceeded the normal saturation values in ten of the twelve 7-minute extracts and in all of the 2-hour extracts. The data do not fall on a smooth curve because the degree of supersaturation undoubtedly varied among the filtrates. Also in the case of the high-potash clinkers the presence of SO_3 may have affected the solubility relations.

A qualitative verification of the supersaturation of the solutions was obtained by visually estimating the amounts of crystalline ma-

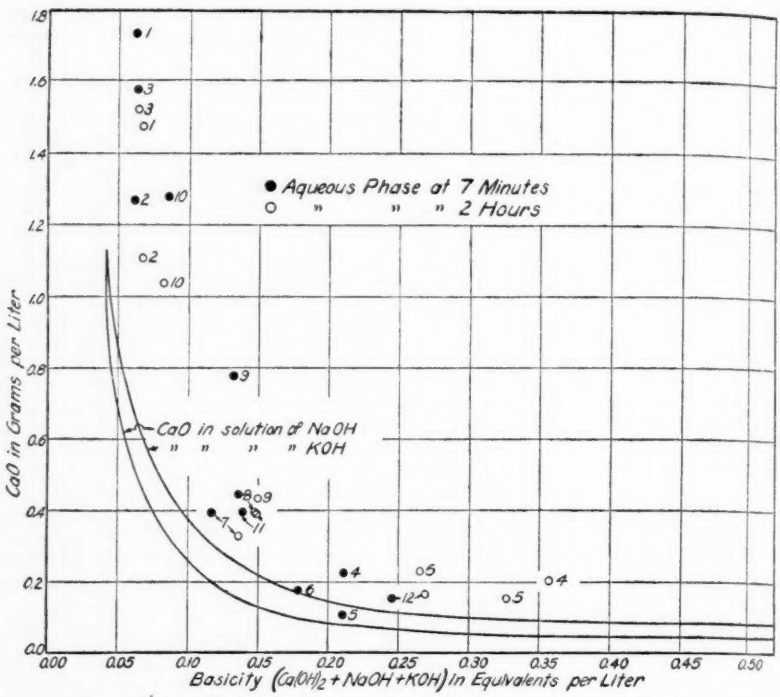
Aqueous Phase at 7 Minutes
" " " 2 Hours
CaO in solution of NaOH
" " " " KOH
CaO in Grams per Liter
Basicity (Ca(OH)2 + NaOH + KOH) in Equivalents per Liter

FIGURE 2.—*Plot of* CaO*-basicity data for filtrates from untreated clinker pastes compared with solubilities of* $Ca(OH)_2$ *in pure solutions of* NaOH *and* KOH *reported by Forsen* [13].

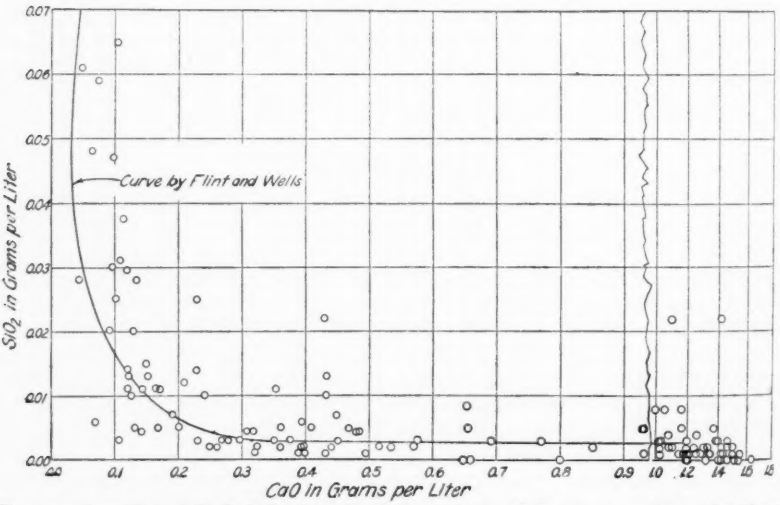

FIGURE 3.—*Plot of* $CaO–SiO_2$ *data for filtrates from clinker pastes with and without added materials compared with the* $CaO–SiO_2$ *correlation reported for the system* $CaO–SiO_2–H_2O$ *by Flint and Wells* [14].

terial precipitated after 2 months from the various filtrates sealed in glass tubes. The crystals, identified as $Ca(OH)_2$, were as much as 1 mm in cross section.

(c) SILICA

Figure 1 shows that an increased concentration of silica in the extracts was accompanied by a decreased concentration of lime. The relation is more evident in figure 3, where the concentration of silica is plotted against that of lime in all of the extracts except those from pastes containing calcium chloride, calcium acetate, and fluosilicic acid. The correlation of the data with the curve given by Flint and Wells [16] for the solubility of silicia in lime solutions at 30° C is noteworthy. Apparently the effect of the alkalies on the lime concentration, illustrated in figure 2, does not greatly alter the silica-lime relation. The spread in the points is not surprising, considering the complex nature of the solutions, the lack of attainment of equilibrium, and relatively large analytical errors in the determination of the small amounts of SiO_2.

Flint and Wells [16] and Bessey [17] have demonstrated that the compositions of the hydrous calcium silicates are dependent on the composition of the solution. Thus, as the concentration of lime in solution is decreased, the precipitated calcium silicate hydrate becomes poorer in lime. The observed correlation of the CaO-SiO_2 data in the present investigation suggests that lime-poor silicates may be precipitated in the clinker pastes as the lime concentration in the solution is decreased.

(d) R_2O_3 GROUP (Al_2O_3, Fe_2O_3, AND Cr_2O_3)

Figure 1 shows that the concentration of R_2O_3 varied from 0.001 to 0.033 g/liter at 7 minutes and from 0.001 to 0.018 g/liter at 2 hours. The 7-minute filtrates showing the highest R_2O_3 contents (from clinker pastes 4, 5, and 6) contained Cr_2O_3; at 2 hours, however, the constituent was present only in the extract from clinker 6. All solutions containing Cr_2O_3 were yellow, indicating the presence of the chromate ion.

The portions of R_2O_3 as Al_2O_3 plus Fe_2O_3 varied from 0.001 to 0.017 g/liter in the filtrates from pastes containing no added materials. When the organic addition agents were incorporated in the pastes, relatively large concentrations of Fe_2O_3 and Al_2O_3 were sometimes obtained. The changes will be discussed in the section dealing with the added materials individually.

(e) SO_3

As shown in figure 1 the SO_3 was present in significant amounts in filtrates from clinker pastes 4, 5, and 6 at 7 minutes, but decreased in the interval between 7 minutes and 2 hours. These decreases appear to be caused by the precipitation of calcium sulfoaluminate according to the reaction:

$$3CaO.Al_2O_3[5]+3K_2SO_4+3Ca(OH)_2+31H_2O=3CaO.Al_2O_3.3CaSO_4.31H_2O+6KOH.$$

The evidence for the occurrence of this reaction is based on calculations which show that the equivalents of $SO_4^=$ precipitated in the interval between 7 minutes and 2 hours are equal to the increase in

[5] The formula $3CaO.Al_2O_3$ is used in this and subsequent equations for purposes of discussion only, since other aluminous materials in cement clinkers may react similarly. The trisulfate form of sulfoaluminate is considered here, but the precipitation of the monosulfate form would not alter the ionic balances.

equivalents of OH^- during the same interval, allowance being made for the OH^- that was introduced by further changes in the concentration of the alkalies and lime. Such calculations were reported in a previous publication [1] for extracts of one of the untreated pastes. The more complete data now available are given in table 5 for the filtrates containing the larger amounts of SO_3 at 7 minutes from clinker pastes alone, and with T D A, tannic acid, and fluosilicic acid as added materials. Table 5 shows that for each filtrate the total increase in OH^- concentration (column 3) exceeds the total decrease in $SO_4^=$ concentration (column 6). This is accounted for by the changes in the concentrations of NaOH, KOH, and $Ca(OH)_2$ in the extracts between 7 minutes and 2 hours. If the OH^- introduced from these sources (column 4) is deducted from the total increase in OH^- concentration (column 3), the increases in OH^- caused by the sulfoaluminate reaction are obtained (column 5). These values are in close agreement with the decreases in $SO_4^=$ concentration (column 6).

TABLE 5.—*Changes in ionic concentrations of extracts from clinker pastes between 7 minutes and 2 hours*

Clinker	Added material	Total increase in OH^-	Increase in OH^- corresponding to changes in K_2O, Na_2O, and CaO	Increase in OH^- caused by sulfoaluminate reaction	Total decrease in $SO_4^=$
		Equiv/liter	*Equiv/liter*	*Equiv/liter*	*Equiv/liter*
4	None	0.145	0.032	0.113	0.113
4	T D A	.141	.020	.121	.121
4	Tannic acid	.245	.083	.162	.149
4	Fluosilicic acid	.214	.066	.148	.158
5	None	.117	.043	.074	.067
5	T D A	.072	.013	.059	.059
5	Tannic acid	.184	.079	.105	.100
5	Fluosilicic acid	.182	.082	.100	.097
6	None	.088	.065	.013	.019
6	T D A	.073	.031	.042	.041
6	Tannic acid	.090	.085	.005	.004
8	T D A	.059	.009	.050	.046
9	do	.040	.005	.035	.034
10	do	.009	.003	.012	.009
12	do	.071	.017	.054	.055

In many instances the sulfoaluminate reaction accounts for the small amounts of SO_3 in the filtrates at 7 minutes. For example, the low concentration of SO_3 (0.10 g/liter) in the 7-minute extract from the paste of clinker 4 containing sucrose suggests that almost complete precipitation of the SO_3 as sulfoaluminate had occurred. In the extract from the corresponding paste containing no added material, the high concentration of SO_3 (7.90 g/liter) leads to the belief that precipitation of sulfoaluminate had proceeded more slowly.

3. pH AND OTHER CONSTANTS OF THE FILTRATES

Constant emf was not attained in many of the pH determinations. This may have been due to the presence of so-called "electrode poisons" (traces of sulfur compounds, ferric and chromate ions, etc.). Although as much as 6 hours was allowed frequently for approaching a constant emf, the values obtained in many determinations appeared to be low. Because of the uncertainty as to the accuracy of such results, and since the filtrates consisted essentially of mixtures of

calcium and alkali hydroxides and their salts, the pH values of pure solutions of calcium hydroxide and potassium hydroxide, respectively, were determined. These values are plotted against corresponding basicities in figure 4. The resulting curves furnish a basis for comparison with the data on filtrates from the clinker pastes, with and without added materials, plotted in the same figure.

The two curves extending from pH 11.95 to 12.53 and from 12.55 to 13.60 are those for pure solutions of calcium hydroxide and potassium hydroxide, respectively. These curves do not meet because potassium hydroxide is the stronger of the two bases and, at an equivalent concentration, has the higher pH. Thus at a basicity of 0.04 equiv/liter, corresponding to that of a saturated lime solution, the curves show a difference in pH of 0.04 unit. However, above about 0.15 equiv/liter, the pH values of solutions containing both hydroxides are practically the same as those shown by the upper curve because of the low solubility of calcium hydroxide in potassium hydroxide solutions. The pH values of the filtrates from the clinker pastes, therefore, show greater deviations from the potassium hydroxide curve at the lower basicities than at the higher.

Figure 4 includes the pH values of practically all filtrates except those containing triethanolamine. The use of this addition agent resulted in such large potential disturbances that emf measurements could not be made. The rather consistently low values obtained on filtrates when TDA was present are also attributed to electrode poisons. Practically all the other low results on the filtrates, except those containing the calcium salts as added materials, may result from the same cause.

The pH values, in the absence of electrode poisons, are approximately represented by the potassium hydroxide curve in figure 4, allowance being made at the lower basicities for the presence of calcium hydroxide in the solutions.

The effect of highly soluble calcium salts in lowering the pH of the extracts by relatively large amounts is illustrated in figure 4, where the pH values of filtrates containing calcium chloride and calcium acetate are seen to lie below the pH curve. These decreases in pH are caused by the decreased effective concentration of the hydroxyl ion in the solutions.

Gypsum, because of its lower solubility, decreased the pH by only 0.02 to 0.04 unit at the basicities prevailing in the extracts.

The excellent agreement between the pH values for $Ca(OH)_2$ solutions, from 0.04 to 0.015 equiv/liter, reported by Lea and Bessey [18] and those reported here is of interest because different methods of calculating pH were employed.

In figure 5 the specific conductivity is plotted against basicity of the filtrates from a representative number of clinker pastes with and without added materials. The relation is approximately linear for most of the extracts consisting essentially of solutions of potassium, sodium, and calcium hydroxides, such as many of the filtrates from the pastes alone and from all of those containing sucrose and triethanolamine. The introduction of relatively large amounts of sulfates, chlorides, or acetates in some of the extracts, resulting from the addition of calcium salts, accounts for the increased conductivity of such solutions.

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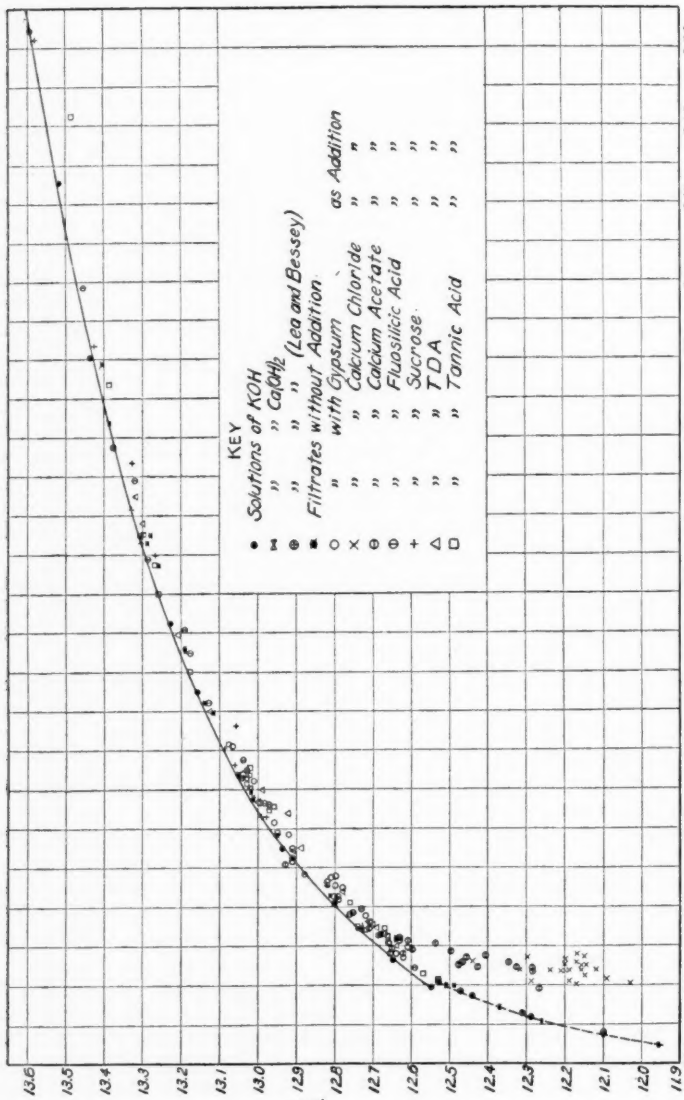

FIGURE 4.—*Plot of* pH-*basicity data for filtrates from clinker pastes with and without added materials compared with the* pH *of pure solutions of* $Ca(OH)_2$ *and* KOH.

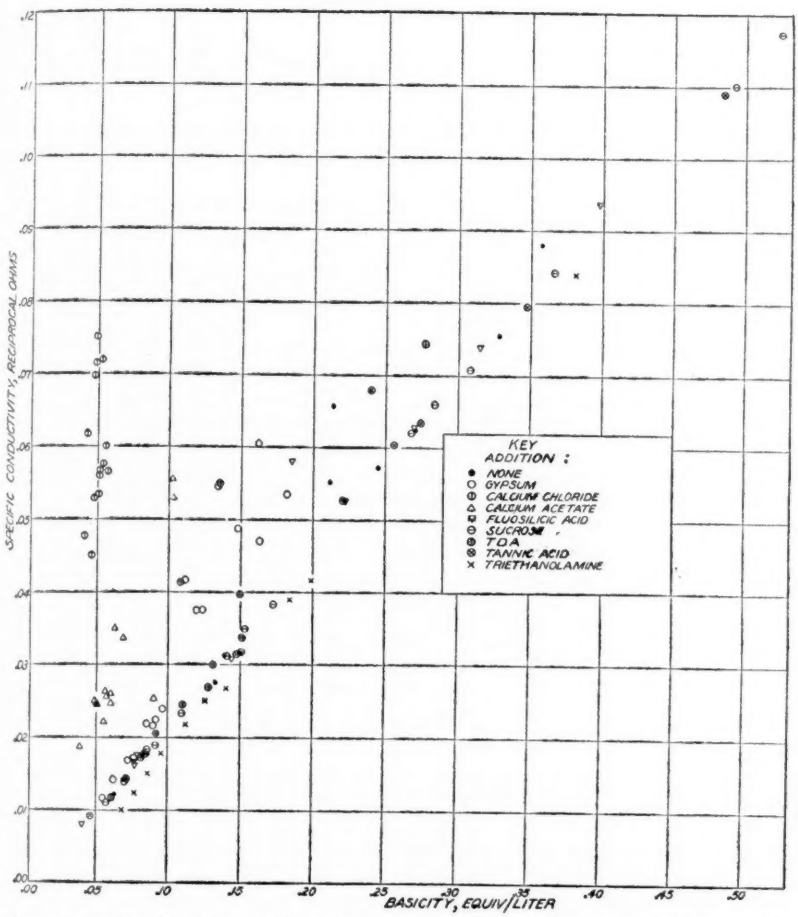

FIGURE 5.—*Conductivity and basicity of filtrates from clinker pastes with and without added materials.*

The densities of the extracts, required for calculating the surface tensions, are included in table 3, in order that the analytical data, if desired, may be expressed on a weight basis.

The surface-tension data, neglecting those below 72.0 dynes/cm, which were known to be low because of the presence of surface contaminants, range from 72.0 to 73.0 dynes/cm. The higher values were obtained on solutions containing calcium chloride and acetate as additions. It has occasionally been suggested that changes in surface tension of the aqueous phase of cement pastes may affect such properties as workability. It seems doubtful, however, that the relatively small observed changes in values could be given much weight in interpreting such properties of the pastes.

4. EFFECTS OF ADDED MATERIALS ON THE COMPOSITIONS OF THE FILTRATES AND ON SOME OF THE REACTIONS IN HYDRATING CLINKERS

The changes in concentrations of the filtrate constituents, caused by the added materials, are shown in figures 6 and 8 to 14. In constructing these figures the differences between the total concentrations of a given constituent in the filtrates from pastes with and without the added material were obtained from the data in table 3. As shown in figure 6, these differences were plotted against the percentages of potash in the clinkers. Identical concentrations of the various constituents in the extracts of the pastes with and without gypsum (fig. 6), for example, are indicated by points on the horizontal lines designated 0, .0, and .00. Increases and decreases are represented by points above and below the lines, respectively.

A uniform scale of plotting the graphs could not be employed because of the widely different changes in concentration of the various filtrate constituents. The scale units for the respective oxides in most cases are

(1) 1.0 g/liter: K_2O, Na_2O, and SO_3.
(2) 0.2 g/liter: CaO.
(3) 0.1 equiv/liter: basicity.
(4) 0.02 g/liter: SiO_2 and R_2O_3.

Departures from these scales were necessary in some of the graphs, and such changes will be pointed out where they occur.

The use of the potash content of the clinkers in these graphs is based on reasons similar to those given in the discussion of figure 1. Figures 6 and 8 to 14 show that in most cases the greater changes, caused by the added materials, occur in the extracts of clinkers having the higher potash contents. Distinct trends in the alterations of all of the filtrate constituents, except soda, are often apparent.

It should be pointed out that small differences between the compositions of filtrates from pastes with and without added materials may not necessarily indicate effects of the additions but may be caused by difficulties in duplicating the manner of mixing the pastes or the time of filtration. Although the time of filtration of duplicate pastes did not vary more than 1 or 2 minutes, as already mentioned, greater variations were experienced in that of pastes made from clinkers with and without added materials. Some of the pastes which became quick-setting in the presence of added materials, had to be mixed more vigorously and often required 2 to 5 minutes longer for filtration than companion pastes without additions.

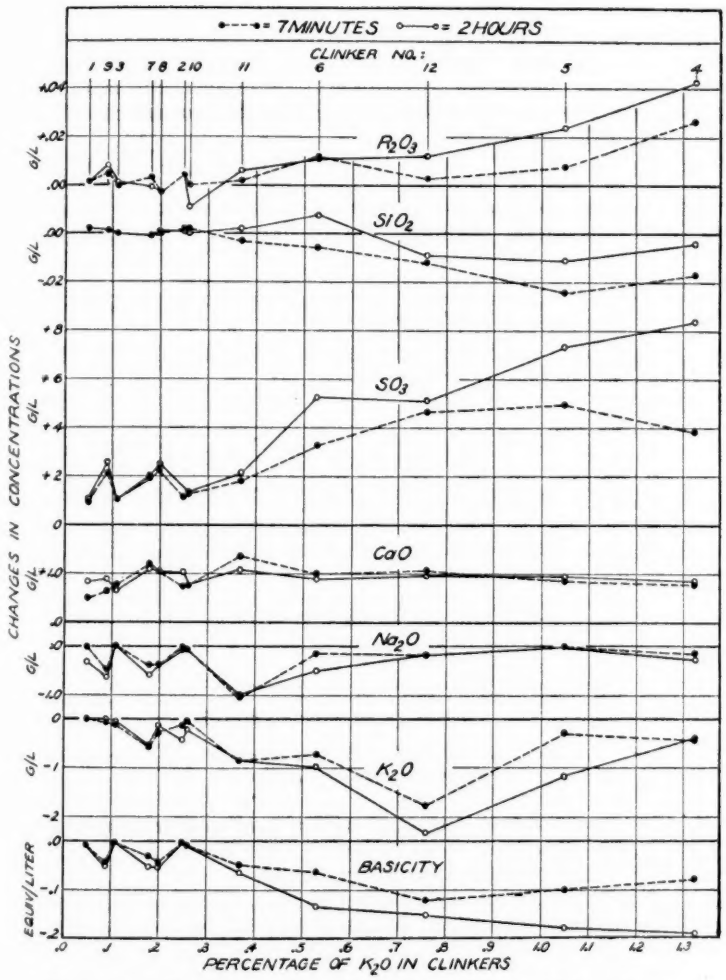

FIGURE 6.—*Changes in compositions of extracts caused by gypsum.*
Note variations in scale.

(a) GYPSUM

The changes in concentration of the filtrate constituents, shown in figure 6, represent differences in composition of the extracts from the cements and the corresponding clinkers. Trends of decreased basicity, lowered concentrations of alkalies and silica, and increased concentrations of lime, sulfate, and R_2O_3 in the extracts of the cements are apparent.

The decrease in basicity and increase in SO_3 concentration of the extracts show rather regular trends of increasing magnitude with increasing potash content of the clinkers. The lowered basicity may be caused in part by the neutralization of alkali hydroxides in the extracts according to the reaction:

$$2KOH \text{ (or } NaOH) + CaSO_4.2H_2O = Ca(OH)_2 + K_2SO_4(Na_2SO_4).$$

A further cause may be the reduced concentration of total potash and soda in the extracts. Comparison of figure 6 with figures 8 to 14

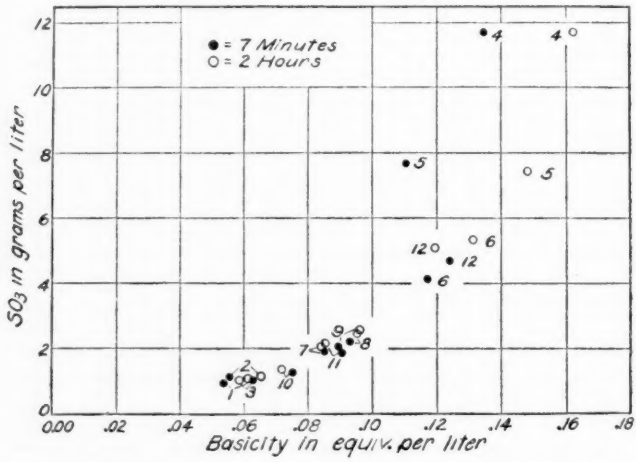

FIGURE 7.—*Plot of SO_3-basicity data of extracts obtained at 7 minutes and 2 hours from pastes containing gypsum.*

shows that gypsum was the only added material which consistently decreased the extraction of the alkalies from the clinkers, although in a few cases the decreases were insignificant.

It may be noted that the above reaction will proceed to the right only if the alkalies dissolve as hydroxides. If they appear in solution as sulfates, the possibility exists that the reaction may proceed to the left. For this reason, it seems that not only the concentrations of the alkali hydroxides but also the possible concentrations of sulfate merit consideration in making interpretations based on the reaction. The relation between basicity and sulfate concentration of the extracts is shown by a plot of the basicity-SO_3 data in figure 7. This figure shows that relatively high basicities may prevail in the extracts even when gypsum is present in the pastes.

Decreases in the concentration of silica and increases in that of R_2O_3 group are indicated in figure 6. As shown by analysis, the increases in the concentrations of R_2O_3 in the extracts from clinkers

4, 5, 6, 9, and 12 were due to the presence of Cr_2O_3. The yellow color of the other filtrates suggests that they also contained Cr_2O_3 but in amounts of less than 0.005 g/liter, this being the lowest concentration detectable by the procedure used.

(b) CALCIUM CHLORIDE

Comparison of the decreases in basicity in the extracts in figures 8 and 6 indicates that calcium chloride produced larger changes than did gypsum. This may be due to the greater solubility of calcium chloride, which permitted more complete neutralization of the alkali hydroxides, according to the equation:

$$2KOH \text{ (or } NaOH) + CaCl_2 = Ca(OH)_2 + 2KCl \text{ (or } NaCl).$$

Calcium chloride also differed from gypsum in that, on the average, it increased the extractions of the alkalies from the clinkers. At 2 hours, particularly, the trend of increased potash concentration is very uniform.

In the presence of calcium chloride, the sulfoaluminate reaction appears to be greatly accelerated, as indicated by the large decreases in SO_3 concentration, leaving only small amounts in solution. The sulfoaluminate may precipitate from pastes of clinkers containing potassium sulfate, according to the reaction:

$$3CaCl_2 + 3K_2SO_4 + 3CaO.Al_2O_3 + 31H_2O = 3CaO.Al_2O_3.3CaSO_4.31H_2O + 6KCl.$$

This reaction would account for the smaller amounts of lime present in the extracts from the clinkers containing potassium sulfate.

The quantities of lime remaining in solution are governed by the extent of precipitation of calcium chloroaluminate as well as by the neutralization and sulfoaluminate reactions. The formation of the chloroaluminate proceeds according to the equation:

$$3CaO.Al_2O_3 + CaCl_2 + 10H_2O = 3CaO.Al_2O_3.CaCl_2.10H_2O.$$

General trends of lowered concentrations of both silica and R_2O_3 occurred in the extracts containing calcium chloride. In most cases the decreases were greater at 7 minutes than at 2 hours.

The decreases in the concentration of the chlorine from that added as calcium chloride (26.62 g of Cl/liter) are attributed largely to the formation of the chloroaluminate. Previous work [7] has shown that the composition of this compound does not vary much from the formula $3CaO.Al_2O_3.CaCl_210H_2O$ in the presence of concentrations of calcium chloride such as prevail in the extracts. Assuming that the chlorine is precipitated only as the chloroaluminate, calculations show that the percentages of the total Al_2O_3 which had reacted were as follows:

Clinker	1	2	3	4	5	6	7	8	9	10	11	12
7 minutes	3.0	3.2	4.8	2.6	2.7	4.2	4.7	5.3	7.3	7.3	4.7	5.3
2 hours	10.1	8.7	9.5	4.3	4.2	6.5	8.9	7.3	10.4	9.6	8.6	7.2

These results indicate that only small amounts of Al_2O_3 reacted with the calcium chloride during the two time periods.

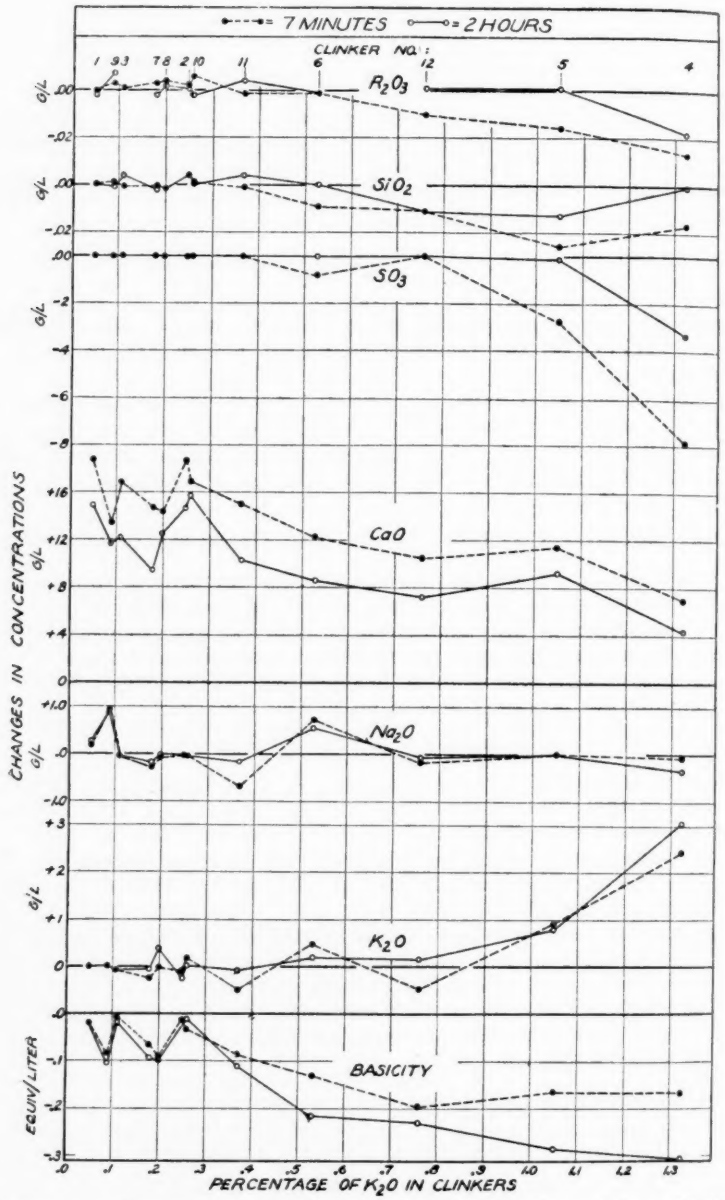

FIGURE 8.—*Changes in compositions of extracts caused by calcium chloride*
Note variations in scale.

(c) CALCIUM ACETATE

The changes caused by the presence of calcium acetate in the extracts are very similar both in magnitude and direction to those induced by calcium chloride as, comparison of figures 9 and 8 will reveal. As before, the basicities of many of the extracts are governed largely by the neutralization reaction between the alkali hydroxides and the added salt. The amounts of lime in the extracts (note reduced scale) are somewhat smaller than those in the extracts containing calcium chloride. It should be noted that smaller amounts of calcium acetate were added to the pastes. The remaining alterations show no marked departures from those produced by calcium chloride, except that some extracts of the low-potash clinkers contained appreciably more R_2O_3 in the presence of calcium acetate.

A white tubid appearance of ten of the twelve 7-minute extracts and of one of the 2-hour extracts indicated that some of the constituents of these solutions were present in the colloidal state.

The acetate added to the pastes was withdrawn from the extracts, probably in part by precipitation as an acetoaluminate [19] and in part by absorption, as indicated by the decreased concentration of acetate in solution at 7 minutes. Although further decreases in acetate concentration occurred between 7 minutes and 2 hours in extracts of five of the clinkers, increases were found in the six remaining extracts. No comparison is possible in the case of clinker 7 because the specified amount of calcium acetate was not added to the 2-hour paste.

(d) FLUOSILICIC ACID

The changes produced by fluosilicic acid were generally small, as shown in figure 10. Fluorine was found in the extracts in amounts varying between 0.00 to 0.11 and 0.00 to 0.18 g/liter at 7 minutes and 2 hours, respectively. The small amounts of fluorine in the extracts at 7 minutes show that the constituents of this material were rapidly precipitated.

The minor alterations in basicity and SO_3 were decreases for the most part. Changes in the extractions of soda were small, but the extractions of potash are of interest in that they were decreased at 7 minutes and altered only slightly at 2 hours. Precipitation of calcium fluoride from the extracts may be indicated by the generally decreased concentration of lime in the extracts at both 7 minutes and 2 hours.

A general trend of decreased silica and increased R_2O_3 concentration in the filtrates is apparent in figure 10.

(e) SUCROSE

Sucrose is the only one of the added materials considered thus far that increased the basicity of the extracts (fig. 11). This was caused not only by increased extraction of the alkalies but also, to a greater extent, by the almost complete conversion of dissolved potassium sulfate to potassium hydroxide, according to the sulfoaluminate reaction. Only 0.03 to 0.15 g/liter of SO_3 remained in the 7-minute extracts of clinkers 4, 5, and 6, which contained the larger amounts of SO_3. At the same time, the lime concentrations of 0.04 to 0.07 g/liter were lower than those corresponding to saturation values for the respective potassium hydroxide concentrations (see fig. 2). The

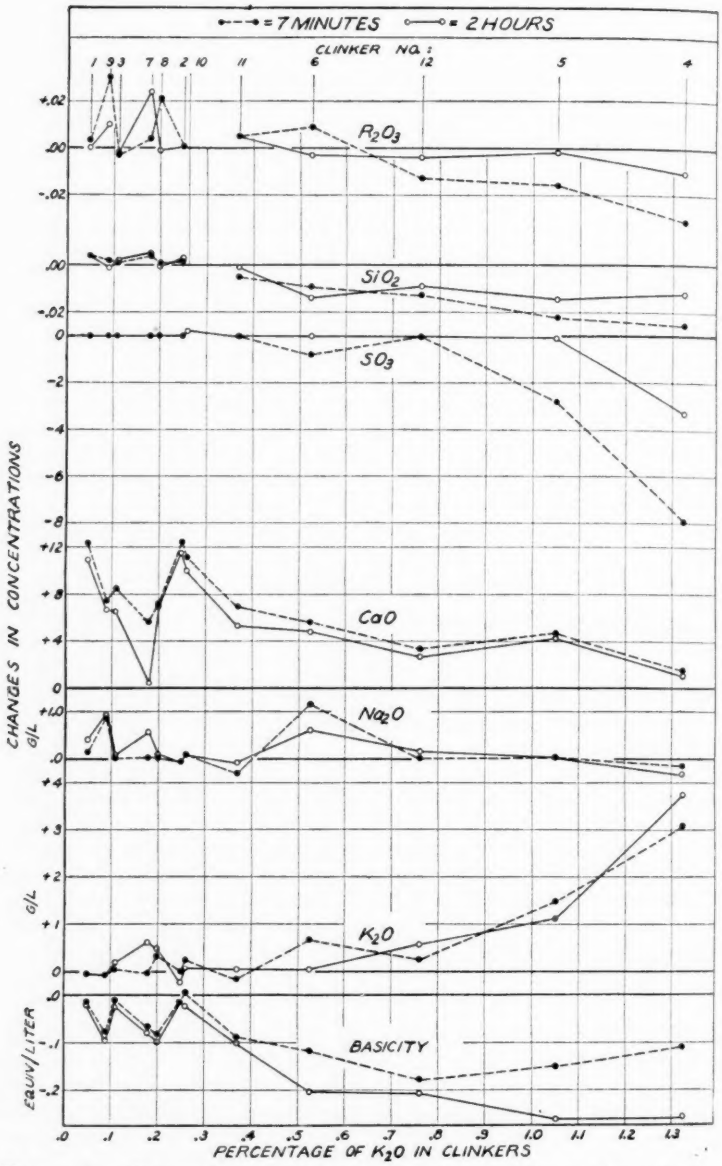

FIGURE 9.—*Changes in compositions of extracts caused by calcium acetate.*

Note variations in scale.

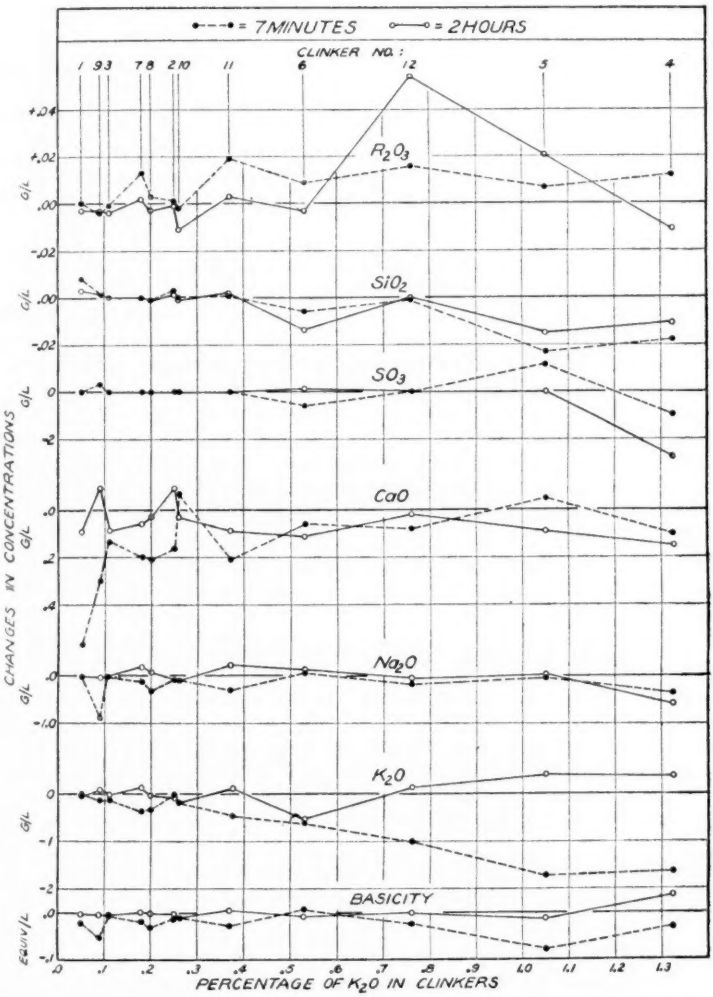

FIGURE 10.—*Changes in compositions of extracts caused by fluosilicic acid.*
Note variations in scale.

large quantities of lime required for the precipitation of the sulfoaluminates may account for the apparent undersaturation. If all the SO_3 were completely extracted from each of the clinkers and precipitated either as the trisulfate form of sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$, or as the monosulfate form, $3CaO.Al_2O_3.CaSO_4.12H_2O$, the amounts of lime and tricalcium aluminate required would be as follows:

Clinker	Total SO_3 in 7,000 g of clinker	Quantities required by sulfoaluminates			
		Trisulfate form		Monosulfate form	
		CaO	$3CaO.Al_2O_3$	CaO	$3CaO.Al_2O_3$
	g	g	g	g	g
4	36	25	40	25	120
5	26	18	29	18	87
6	13	9	14	9	42

The large increases in the amounts of R_2O_3, consisting wholly of alumina, in the 7-minute extracts of clinkers 4, 5, and 6 may therefore be due to the low-lime concentration in these filtrates. This suggestion is supported by the observation that, as the CaO concentration increased in the interval between 7 minutes and 2 hours, the alumina concentration decreased to values approximating those of untreated filtrates. The alumina was precipitated, presumably, as a calcium aluminate hydrate, although the reactions of the aluminous compounds in the clinker after the sulfate had combined as a sulfoaluminate are not yet definitely known. On the basis of recent results [20], both the monosulfate and trisulfate sulfoaluminates are metastable in the presence of alkali hydroxide (0.1 to 0.5 *N*), with respect to members of the solid-solution series,

$$3CaO.Al_2O_3.CaSO_4.12H_2O—3CaO.Al_2O_3.Ca(OH)_2.12H_2O.$$

Therefore, as the aluminous compounds continue to react, the basicity having increased due to the sulfoaluminate reaction involving potash, a conversion of the metastable products to members of the solid-solution series might be expected. However, this conversion occurs but slowly, and, therefore, calcium aluminate hydrate is probably precipitated as such during the period between 7 minutes and 2 hours considered here.

Figure 11 shows that the changes in the concentration of silica were small except in the extracts from clinkers 1 and 4.

(f) T D A

Of the various added materials, T D A (plus 0.23 percent of H_2O) resembles gypsum the most closely in its effects on the extracts. For example, comparison of figures 12 and 6 reveals a striking similarity in the graphs showing changes in the concentration of potash.

The decreases in the basicity of the extracts are caused partially by the reduced extractions of the alkalies but perhaps to an even greater extent by inhibition of the sulfoaluminate reaction. This appears to be indicated ir figure 12 by increases in the concentration of SO_3 in the extracts over those prevailing in the filtrates from pastes without added

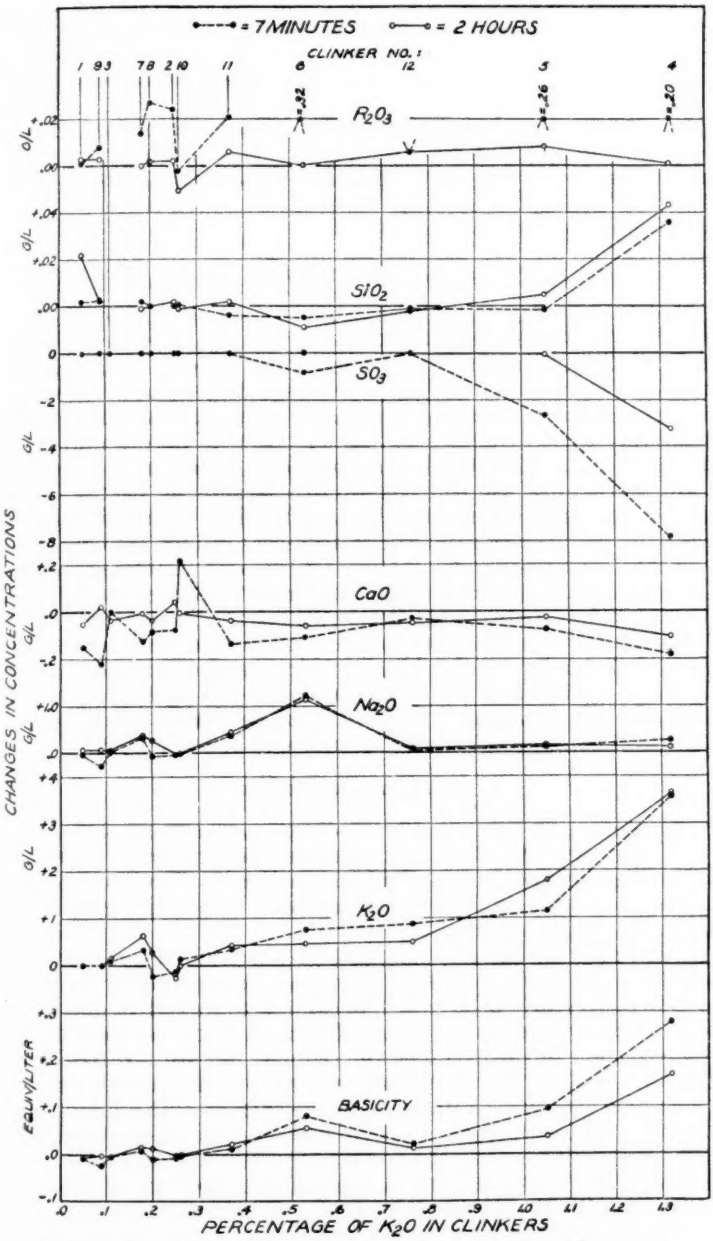

FIGURE 11.—*Changes in compositions of extracts caused by sucrose.*
Note variations in scale

materials. Although the reason for the retardation of this reaction is not apparent, the addition of 0.23 percent of water during the incorporation of the T D A may have partially prehydrated the clinker. Such prehydration would have been possible, since the T D A (plus 0.23 percent of H_2O) was mixed with each clinker on the day preceding the tests.

At 7 minutes, figure 12 shows a trend toward a decreased concentration of silica in the T D A-containing extracts, but at 2 hours no significant changes are revealed. The amounts of R_2O_3, which consisted partially of Fe_2O_3 and in some cases Cr_2O_3, were increased in most filtrates at both time periods.

(g) TANNIC ACID

Figure 13 indicates that the changes in composition of the filtrates caused by the addition of tannic acid to the pastes were generally small. At 7 minutes, irregular changes in basicity and potash concentration occur, but at 2 hours fairly regular increases are apparent. The variations in extractions of soda are small at both time periods.

Relatively large decreases in concentration of lime occurred in the 7-minute extracts of a number of low-potash clinkers. Very similar changes were noted in the 7-minute extracts of pastes to which fluosilicic acid had been added (fig. 10). The 2-hour filtrates from pastes with tannic acid show small decreases in lime concentration.

At both 7 minutes and 2 hours, tannic acid produced no change in the concentration of SO_3 in the majority of the extracts. In the remainder, small increases or decreases occur.

The alterations in the concentration of silica are somewhat irregular at both 7 minutes and 2 hours but increases predominate. Relatively large increases in the R_2O_3 content of the extracts were found, particularly at 7 minutes. These increases may result from the formation of complexes between tannic acid and the R_2O_3.

(h) TRIETHANOLAMINE

Triethanolamine produced greater alterations in the compositions of the extracts than any other added material. Because of rapid setting, extracts of 6 of the 12 pastes at 7 minutes and of 2 pastes at 2 hours could not be obtained. Hence the graphs shown in figure 14 are incomplete.

The increases in basicity displayed by a majority of the extracts appear to be caused by greatly increased extractions of the alkalies. Attention has already been called, in table 4, to this effect of triethanolamine. Where the concentrations of alkali hydroxides were increased, the lime content of the extracts was reduced but still exceeded normal saturation values. No significant alteration of the SO_3 concentration occurred except for a decrease in the extract of the clinker highest in potash. Three extracts showed increases in silica concentration of 0.02 to 0.03 g/liter, but the remainder were unchanged.

Probably the most striking change in composition of the extracts is the increase in their content of R_2O_3. The reduced scale on which R_2O_3 is plotted in figure 14 should be noted. As in the case of tannic acid, the increases in concentration of R_2O_3 may result from the formation of complexes between triethanolamine and ferric and aluminum hydroxides.

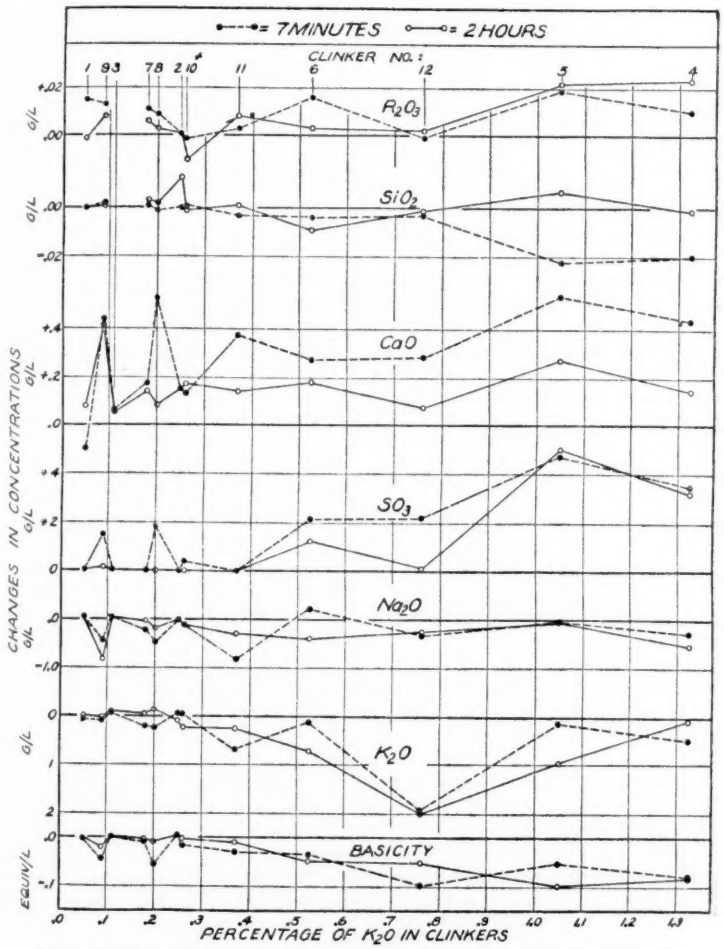

FIGURE 12.—*Changes in compositions of extracts caused by T D A.*
Note variations in scale.

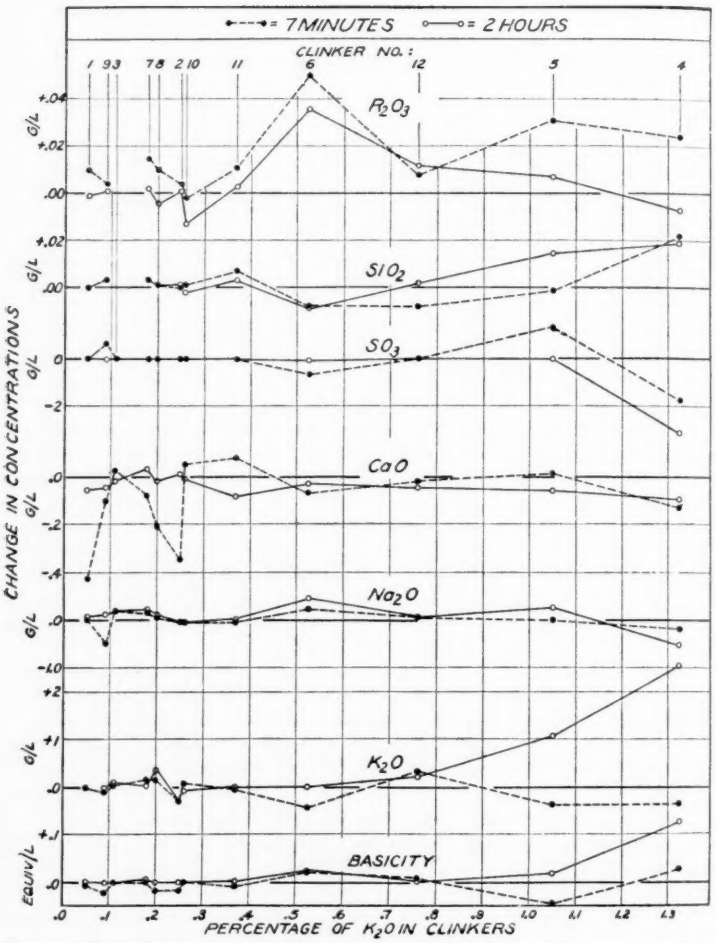

FIGURE 13.—*Changes in compositions of extracts caused by tannic acid.*
Note variations in scale.

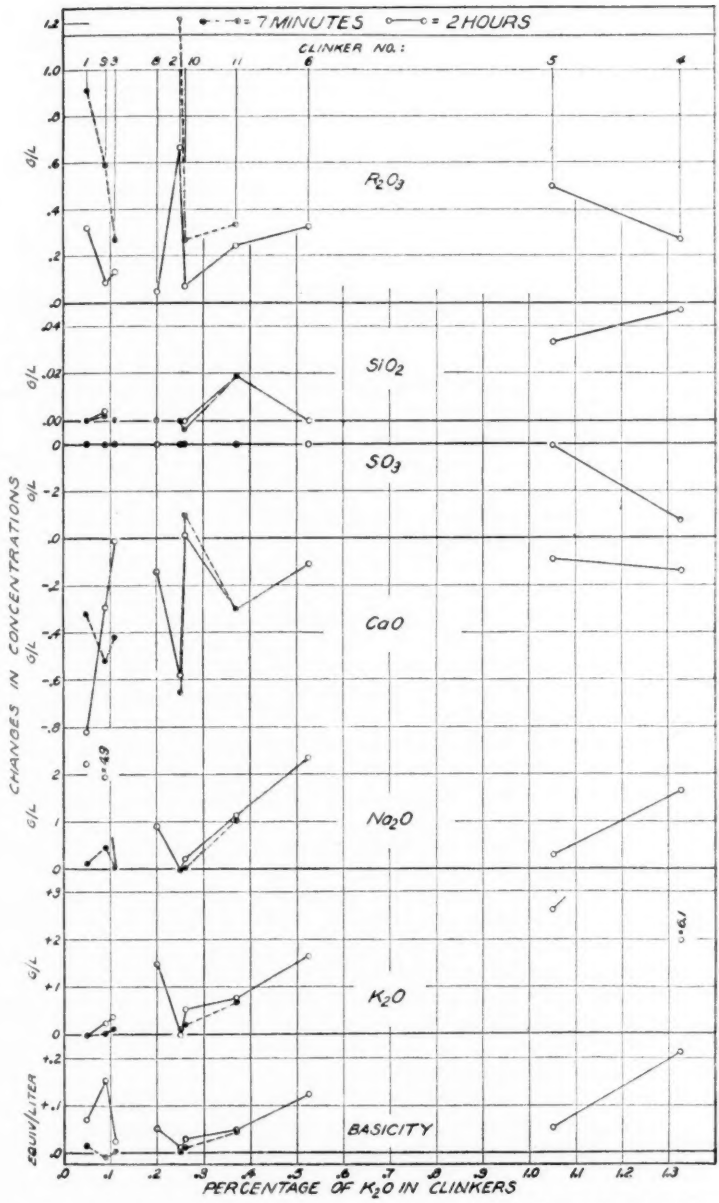

FIGURE 14.—*Changes in composition of extracts caused by triethanolamine.*
Note variations in scale.

508748—43——7

V. SUMMARY

1. From 1 to 58 percent of the total potash and from 0.4 to 30 percent of the total soda in 12 portland cement clinkers were extracted in 7 minutes from pastes of these clinkers containing no added materials. In the interval between 7 minutes and 2 hours the percentage increases in the amounts of potash ranged from 0 to 9 and from 1 to 12 for soda.

Triethanolamine increased the extraction of the alkalies from the clinkers much more than any other material, and gypsum caused the greatest decreases.

2. The extracts of the clinker pastes generally contained lime in amounts greater than the normal saturation values for calcium hydroxide. The exceptions, in a few of the sucrose-containing extracts, were apparently caused by rapid precipitation of calcium sulfoaluminate.

3. The amounts of silica and lime in the extracts corresponded approximately to their reported solubility relations in the system lime-silica-water at 30° C.

4. The amounts of alumina in solution were small except when organic materials had been added to the pastes. Ferric oxide was either absent or present only in small amounts, except in filtrates containing triethanolamine. Small quantities of chromic oxide were found in some of the filtrates.

5. SO_3 usually decreased in concentration between 7 minutes and 2 hours, precipitating as a sulfoaluminate. In some instances, the changes in concentrations of lime and alumina and the increases in basicity were attributed to the formation of calcium sulfoaluminate.

6. Notwithstanding the presence of gypsum, a large spread (0.05 to 0.16 equiv/liter) in basicity was shown by the filtrates from pastes containing added gypsum.

7. Computations based on the amounts of calcium chloride that had combined with alumina in the clinkers up to 7 minutes and 2 hours suggest that only small amounts of the alumina-bearing materials had reacted.

8. Sucrose accelerated the early reactions involving the alumina-bearing constituents of the clinkers.

9. Graphs were constructed to show the pH of pure solutions of calcium and potassium hydroxides. The pH-basicity values of filtrates obtained from clinker-water mixtures, with and without added materials, except calcium salts, approached closely to those of the potassium hydroxide curve when electrode poisons were absent.

The emf cell, used for measuring the pH of the solutions and filtrates, was calibrated against potassium hydroxide solutions of known pH and concentration.

As shown by pH measurements, the presence of calcium chloride and calcium acetate in the filtrates caused large decreases in the effective concentration of hydroxyl ion. The addition of gypsum, on the other hand, caused only slight decreases, which amounted to 0.02 to 0.04 pH unit.

10. The conductivities, surface tensions, and densities of the filtrates are reported.

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